PRO/II Unit Operations Reference Manual

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Credits

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Introduction

General Information

The *PRO/II Unit Operations Reference Manual* provides details on the basic equations and calculation techniques used in the PRO/II simulation program. It is intended as a complement to the *PRO/II Keyword Input Manual*, providing a reference source for the background behind the various PRO/II calculation methods.

What is in This Manual?

This manual contains the correlations and methods used for the various unit operations, such as the Inside/Out and Chemdist column solution algorithms.

For each method described, the basic equations are presented, and appropriate references provided for details on their derivation. General application guidelines are provided, and, for many of the methods, hints to aid solution are supplied.

Who Should Use This Manual?

For novice, average, and expert users of PRO/II, this manual provides a good overview of the calculation modules used to simulate a single unit operation or a complete chemical process or plant. Expert users can find additional details on the theory presented in the numerous references cited for each topic. For the novice to average user, general references are also provided on the topics discussed, e.g., to standard textbooks.

Specific details concerning the coding of the keywords required for the PRO/II input file can be found in the *PRO/II Keyword Input Manual*. Detailed sample problems are provided in the *PRO/II Application Briefs Manual* and in the *PRO/II Casebooks.*

Finding What you Need

A Table of Contents and an Index are provided for this manual. Cross-references are provided to the appropriate section(s) of the *PRO/II Keyword Input Manual* for help in writing the input files.

Symbols Used in This Manual

Symbol	*Meaning*
	Indicates a PRO/II input coding note. The number beside the symbol indicates the section in the *PRO/II Keyword Input Manual* to refer to for more information on coding the input file.
	Indicates an important note.
	Indicates a list of references.

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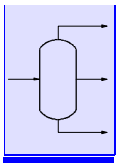
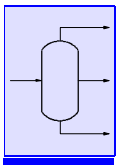


2.1 Flash Calculations

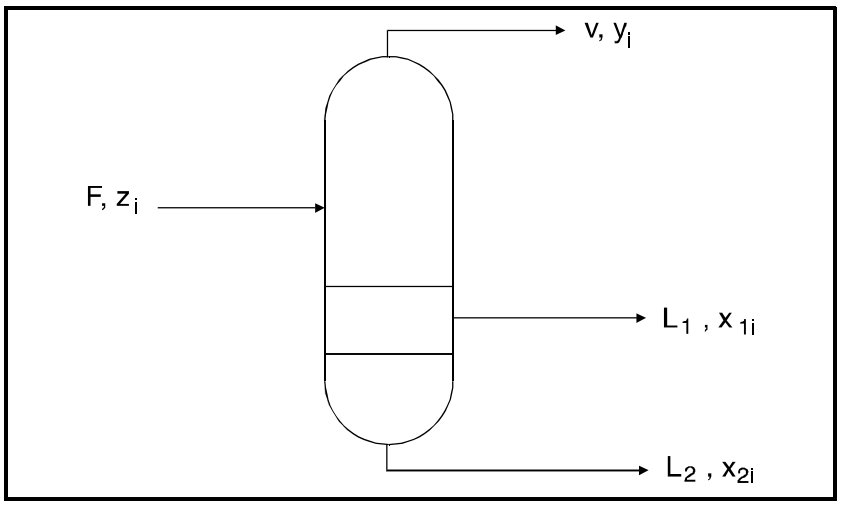
PRO/II contains calculations for equilibrium flash operations such as flash drums, mixers, splitters, and valves. Flash calculations are also used to determine the thermodynamic state of each feed stream for any unit operation. For a flash calculation on any stream, there are a total of NC + 3 degrees of freedom, where NC is the number of components in the stream. If the stream composition and rate are fixed, then there are 2 degrees of freedom that may be fixed. These may, for example, be the temperature and pressure (an isothermal flash). In addition, for all unit operations, PRO/II also performs a flash calculation on the product streams at the outlet conditions. The difference in the enthalpy of the feed and product streams constitutes the net duty of that unit operation.



2.1.1 Basic Principles

Figure 2.1.1-1 shows a three-phase equilibrium flash.

Figure 2.1.1-1: Three-phase Equilibrium Flash



MESH Equations

The Mass balance, Equilibrium, Summation, and Heat balance (or MESH) equations which may be written for a three-phase flash are given by:

Total Mass Balance:

$$F = V + L_1 + L_2 \tag{1}$$

Component Mass Balance:

$$Fz_i = Vy_i + L_1 + L_2 \tag{2}$$

Equilibrium:

$$y_i = K_{1i}\, x_{1i} \tag{3}$$

$$y_i = K_{2i}\, x_{2i} \tag{4}$$

$$x_{1i} = \frac{K_{2i}}{K_{1i}}\, x_{2i} \tag{5}$$

Summations:

$$\sum_i y_i - \sum_i x_{1i} = 0 \tag{6}$$

$$\sum_i y_i - \sum_i x_{2i} = 0 \tag{7}$$

Heat Balance:

$$FH_f + Q = VH_v + L_1H_{1l} + L_2H_{2l} \tag{8}$$

Two-phase Isothermal Flash Calculations

For a two-phase flash, the second liquid phase does not exist, i.e., $L_2 = 0$, and $L_1 = L$ in equations (1) through (8) above. Substituting in equation (2) for L from equation (1), we obtain the following expression for the liquid mole fraction, x_i:

$$x_i = \frac{z_i}{(K_i - 1)\frac{V}{F} + 1} \tag{9}$$

The corresponding vapor mole fraction is then given by:

$$y_i = K_i x_i \tag{10}$$

The mole fractions, x_i and y_i sum to 1.0, i.e.:

$$\sum_i x_i = \sum_i y_i = 1.0 \tag{11}$$

However, the solution of equation (11) often gives rise to convergence difficulties for problems where the solution is reached iteratively. Rachford and Rice in 1952 suggested that the following form of equation (11) be used instead:

$$\sum_i y_i - \sum_i x_i = \sum_i \frac{(K_i - 1)\, z_i}{(K_i - 1)\frac{V}{F} + 1} \le TOL \tag{12}$$

Equation (12) is easily solved iteratively by a Newton-Raphson technique, with V/F as the iteration variable.

Figure 2.1.1-2 shows the solution algorithm for a two-phase isothermal flash, i.e., where both the system temperature and pressure are given. The following steps outline the solution algorithm.

1. The initial guesses for component K-values are obtained from ideal K-value methods. An initial value of V/F is assumed.
2. Equations (9) and (10) are then solved to obtain x_i's and y_i's.
3. After equation (12) is solved within the specified tolerance, the composition convergence criteria are checked, i.e., the changes in the vapor and liquid mole fraction for each component from iteration to iteration are calculated:

$$\frac{|\,(y_{i,ITER} - y_{i,ITER-1})\,|}{y_i} \le TOL \tag{13}$$

Figure 2.1.1-2: Flowchart for Two-phase T, P Flash Algorithm

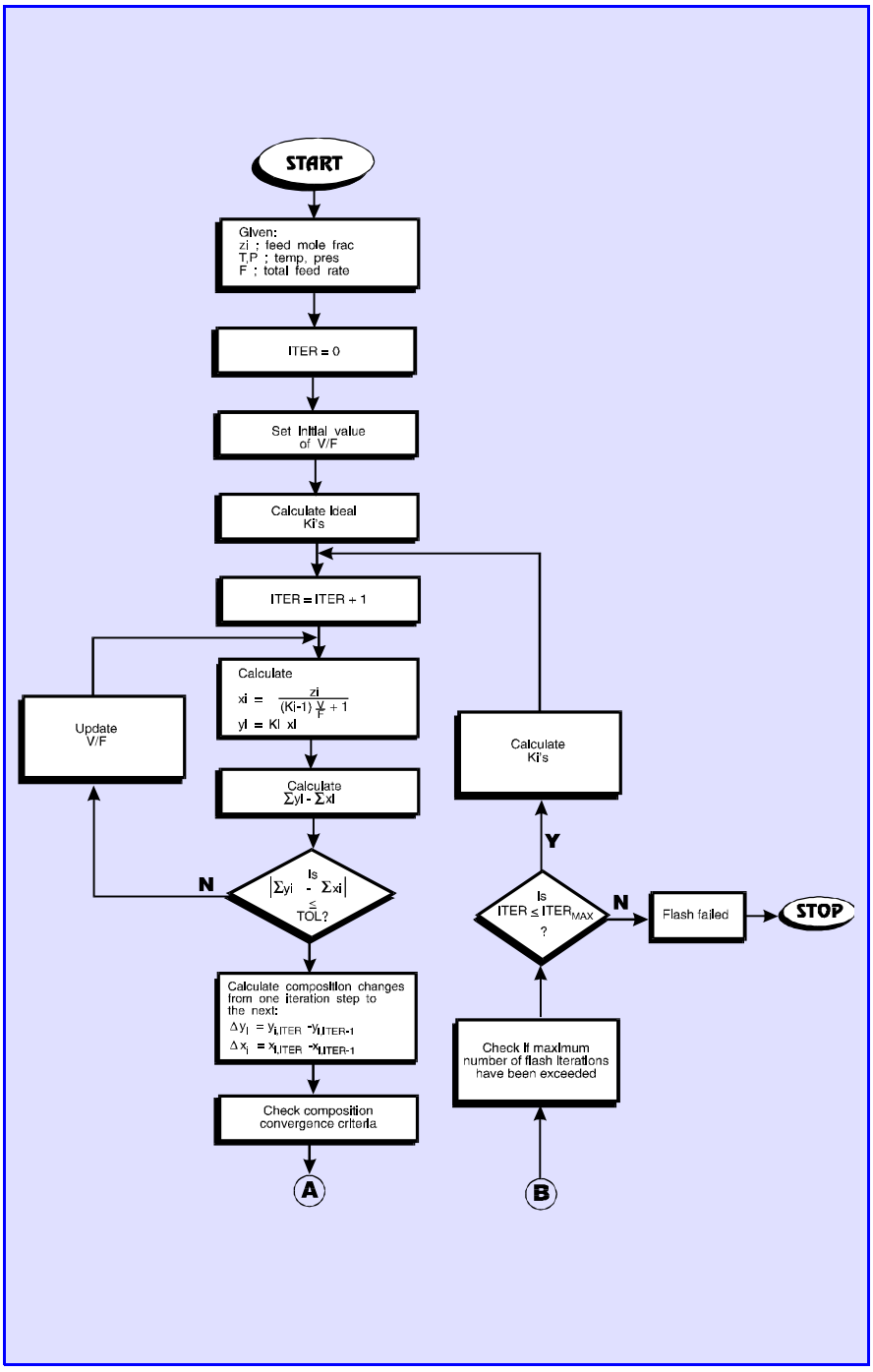
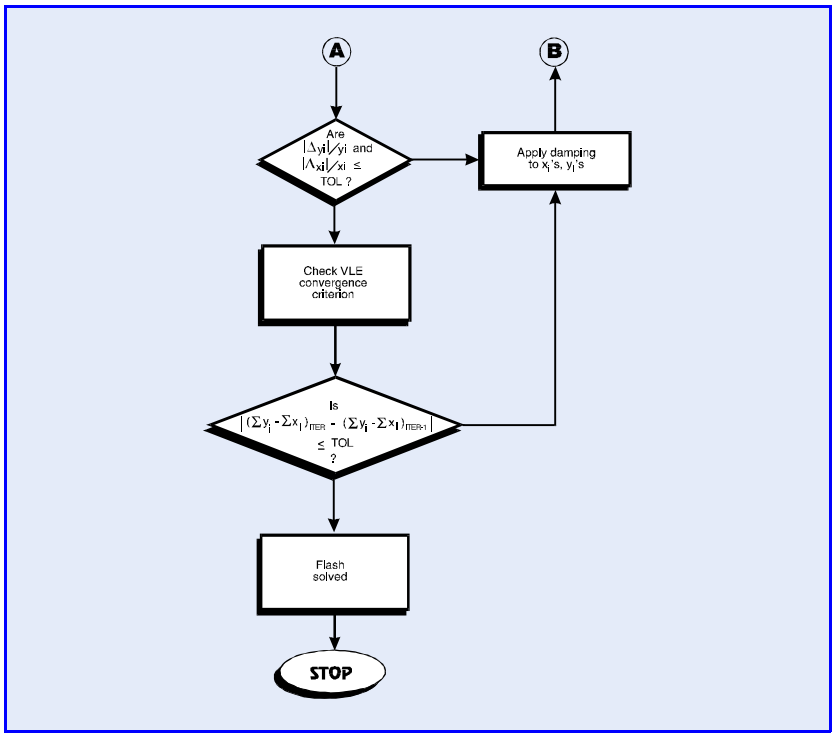


Figure 2.1.1-2:, continued Flowchart for Two-phase T, P Flash Algorithm


A
B
Are |Δyi|/yi and |Δxi|/xi ≤ TOL ?
Apply damping to xi's, yi's
Check VLE convergence criterion
Is |(Σyi - Σxi)ITER - (Σyi - Σxi)ITER-1| ≤ TOL ?
Flash solved
STOP

$$\frac{|(x_{i,ITER} - x_{i,ITER-1})|}{x_i} \leq TOL \qquad (14)$$

4. If the compositions are still changing from one iteration to the next, a damping factor is applied to the compositions in order to produce a stable convergence path.

5. Finally, the VLE convergence criterion is checked, i.e., the following condition must be met:

$$\left| \left(\sum y_i - \sum x_i \right)_{ITER} - \left(\sum y_i - \sum x_i \right)_{ITER-1} \right| \leq TOL \qquad (15)$$

   If the VLE convergence criterion is not met, the vapor and liquid mole fractions are damped, and the component K-values are re-calculated. Rigorous K-values are calculated using equation of state methods, generalized correlations, or liquid activity coefficient methods.

6. A check is made to see if the current iteration step, ITER, is greater than the maximum number of iteration steps $ITER_{max}$. If ITER > $ITER_{max}$, the flash has failed to reach a solution, and the calculations stop. If ITER < $ITER_{max}$, the calculations continue.

7. Steps 2 through 6 are repeated until the composition convergence criteria and the VLE criterion are met. The flash is then considered solved.

8. Finally, the heat balance equation (8) is solved for the flash duty, Q, once V and L are known.

Flash Tolerances

The flash equations are solved within strict tolerances. All these tolerances are built into the PRO/II flash algorithm, and may not be input by the user. Table 2.1.1-1 shows the values of the tolerances used in the algorithm for the Rachford-Rice equation (12), the composition convergence equations (13) and (14), and the VLE convergence equation (15).

Table 2.1.1-1: Flash Tolerances

Equation	Tolerance
Rachford-Rice (12)	1.0e-05
Composition Convergence (13-14)	1.0e-03
VLE Convergence (15)	1.0e-05

Bubble Point Flash Calculations

For bubble point flashes, the liquid phase component mole fractions, x_i, still equal the component feed mole fraction, z_i. Moreover, the amount of vapor, V, is equal to zero. Therefore, the relationship to be solved is:

$$\sum_i K_i z_i = \sum_i y_i = 1.0 \qquad (16)$$

The bubble point temperature or pressure is to be found by trial-and-error Newton-Raphson calculations, provided one of them is specified.

The K-values between the liquid and vapor phase are calculated by the thermodynamic method selected by the user. Equation (16) can, however, be highly non-linear as a function of temperature as K-values typically vary as exp(1/T). For bubble point temperature calculations, where the pressure and feed compositions has been given, and only the temperature is to be determined, equation (16) can be rewritten as:

$$\ln\left\{\sum_i K_i z_i\right\} = 0 \qquad (17)$$

Equation (17) is more linear in behavior than equation (16) as a function of temperature, and so a solution can be achieved more readily.

Equation (16) behaves in a more linear fashion as a function of pressure as the K-values vary as 1/P. For bubble point pressure calculations, where the temperature and feed compositions have been given, the equation to be solved can be written as:

$$\sum_i K_i z_i - 1 = 0 \qquad (18)$$

Dew Point Flash Calculations

A similar technique is used to solve a dew point flash. The amount of vapor, V, is equal to 1.0. Simplification of the mass balance equations result in the following relationship:

$$\sum_i z_i / K_i = \sum_i x_i = 1.0 \qquad (19)$$

For dew point pressure calculations, equation (19) can be linearized by writing it as :

$$\ln\left\{\sum_i \frac{z_i}{K_i}\right\} = 0 \qquad (20)$$

For dew point temperature calculations, equation (19) may be rewritten as:

$$\sum_i \frac{z_i}{K_i} - 1 = 0 \qquad (21)$$

The dew point temperature or pressure is then found by trial-and-error Newton-Raphson calculations using equations (20) or (21).

Two-phase Adiabatic Flash Calculations

For a two-phase, adiabatic (Q=0) system, the heat balance equation (8) can be rewritten as:

$$1 - \frac{H_v}{H_f} - \left(1 - \frac{V}{F}\right)\frac{H_l}{H_f} \le TOL \qquad (22)$$

An iterative Newton-Raphson technique is used to solve the Rachford-Rice equation (12) simultaneously with equation (22) using V/F and temperature as the iteration variables.

Water Decant

The water decant option in PRO/II is a special case of a three-phase flash. If this option is chosen, and water is present in the system, a pure water phase is decanted as the second liquid phase, and this phase is not considered in the equilibrium flash computations. This option is available for a number of thermodynamic calculation methods such as Soave-Redlich-Kwong or Peng-Robinson.

Note: The free-water decant option may only be used with the Soave-Redlich-Kwong, Peng-Robinson, Grayson-Streed, Grayson-Streed-Erbar, Chao-Seader, Chao-Seader-Erbar, Improved Grayson-Streed, Braun K10, or Benedict-Webb-Rubin-Starling methods. Note that water decant is automatically activated when any one of these methods is selected.

The water-decant flash method as implemented in PRO/II follows these steps:

1. Water vapor is assumed to form an ideal mixture with the hydrocarbon vapor phase.
2. Once either the system temperature, or pressure is specified, the initial value of the iteration variable, V/F is selected and the water partial pressure is calculated using one of two methods.
3. The pressure of the system, P, is calculated on a water-free basis, by subtracting the water partial pressure.
4. A pure water liquid phase is formed when the partial pressure of water reaches its saturation pressure at that temperature.
5. A two phase flash calculation is done to determine the hydrocarbon vapor and liquid phase conditions.
6. The amount of water dissolved in the hydrocarbon-rich liquid phase is computed using one of a number of water solubility correlations.
7. Steps 2 through 6 are repeated until the iteration variable is solved within the specified tolerance.

20.6

PRO/II Note: For more information on using the free-water decant option, see Section 20.6, *Free-Water Decant Considerations*, of the *PRO/II Keyword Input Manual*.

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1. Perry R. H., and Green, D.W., 1984, Chemical Engineering Handbook, 6th Ed., McGraw-Hill, N.Y.
2. Rachford, H.H., Jr., and Rice, J.D., 1952, *J. Petrol. Technol.*, **4** sec.1, 19, sec. 2,3.
3. Prausnitz, J.M., Anderson, T.A., Grens, E.A., Eckert, C.A., Hsieh, R., and O'Connell, J.P., 1980, *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria*, Prentice-Hall, Englewood Cliffs, N.J.

Three-phase Flash Calculations

For three-phase flash calculations, with a basis of 1 moles/unit time of feed, F, the MESH equations are simplified to yield the following two nonlinear equations:

$$| f_1(L_1, L_2) | = | \sum_i a_i z_i / d_i | \leq tolerance \quad (23)$$

$$| f_1(L_1, L_2) | = | \sum_i b_i z_i / d_i | \leq tolerance \quad (24)$$

where:

$$a_i = (1 - K_{1i}) \quad (25)$$

$$b_i = (1 - K_{2i}) (K_{1i} / K_{2i}) \quad (26)$$

$$d_i = K_{1i} + a_i L_1 + b_i L_2 \quad (27)$$

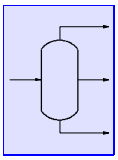
Equations (23) through (27) are solved iteratively using a Newton-Raphson technique to obtain L_1 and L_2. The solution algorithm developed by SimSci is able to rigorously predict two liquid phases. This algorithm works well even near the plait point, i.e., the point on the ternary phase diagram where a single phase forms.

Table 2.1.1-1 shows the thermodynamic methods in PRO/II which are able to handle VLLE calculations. For most methods, a single set of binary interaction parameters is inadequate for handling both VLE and LLE equilibria. The PRO/II databanks contain separate sets of binary interaction parameters for VLE and LLE equilibria for many of the thermodynamic methods available in PRO/II, including the NRTL and UNIQUAC liquid activity methods. For best results, the user should always ensure that separate binary interaction parameters for VLE and LLE equilibria are provided for the simulation.

Table 2.1.1-1:
VLLE Predefined Systems and K-value Generators

K-value Method		System	
SRK[1]	AMINE	SRK[1]	NRTL
SRKM	NRTL	SRKM	UNIQUAC
SRKKD	UNIQUAC	SRKKD	UNIFAC
SRKH	UNIFAC	SRKH	UFT1
SRKP	UFT1	SRKP	UFT2
SRKS	UFT2	SRKS	UFT3
PR[1]	UFT3	PR[1]	UNFV
PRM	UNFV	PRM	VANLAAR
PRH	VANLAAR	PRH	MARGULES
PRP	MARGULES	PRP	REGULAR
UNIWAALS	REGULAR	UNIWAALS	FLORY
IGS	FLORY	IGS	ALCOHOL
GSE	SOUR	GSE	GLYCOL
CSE	GPSWATER	CSE	SOUR
HEXAMER	LKP	AMINE	GPSWATER
		HEXAMER	LKP

[1] VLLE available, but not recommended



2.1.2 Equilibrium Unit Operations

Flash Drum

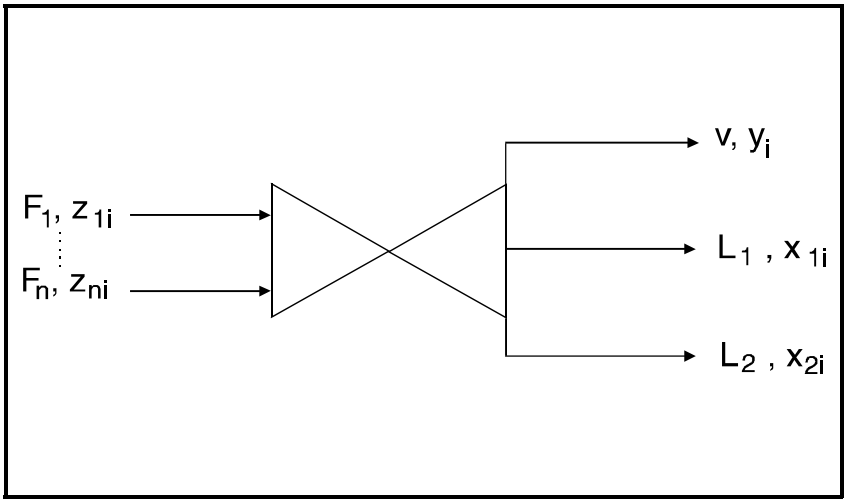
The flash drum unit can be operated under a number of different fixed conditions; isothermal (temperature and pressure specified), adiabatic (duty specified), dew point (saturated vapor), bubble point (saturated liquid), or isentropic (constant entropy) conditions. The dew point may also be determined for the hydrocarbon phase or for the water phase. In addition, any general stream specification such as a component rate or a special stream property such as sulfur content can be made at either a fixed temperature or pressure. For the flash drum unit, there are two other degrees of freedom which may be set by imposing external specifications. Table 2.1.2-1 shows the 2-specification combinations which may be made for the flash unit operation.

Table 2.1.2-1:
Constraints in Flash Unit Operation

Flash Operation	Specification 1	Specification 2
ISOTHERMAL	TEMPERATURE	PRESSURE
DEW POINT	TEMPERATURE PRESSURE	V=1.0 V=1.0
BUBBLE POINT	TEMPERATURE PRESSURE	V=0.0 V=0.0
ADIABATIC	TEMPERATURE PRESSURE	FIXED DUTY FIXED DUTY
ISENTROPIC	TEMPERATURE PRESSURE	FIXED ENTROPY FIXED ENTROPY
TPSPEC	TEMPERATURE PRESSURE	GENERAL STREAM SPECIFICATION GENERAL STREAM SPECIFICATION

Valve

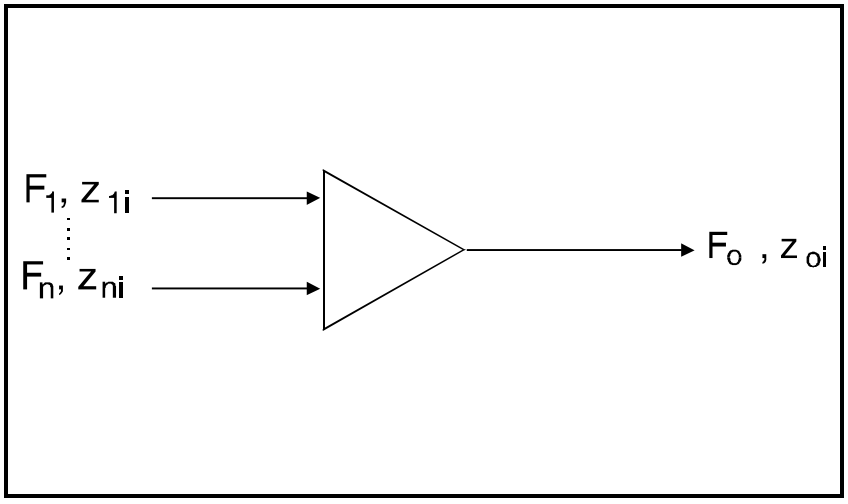
Figure 2.1.2-1: Valve Unit



The valve unit operates in a similar manner to an adiabatic flash. The outlet pressure, or the pressure drop across the valve is specified, and the temperature of the outlet streams is computed for a total duty specification of 0. The outlet product stream may be split into separate phases. Both VLE and VLLE calculations are allowed for the valve unit. One or more feed streams are allowed for this unit operation.

Mixer

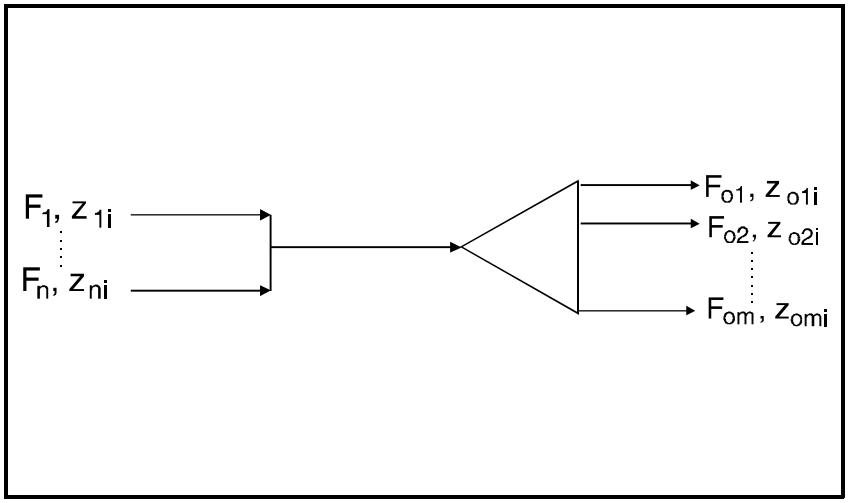
Figure 2.1.2-2: Mixer Unit



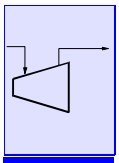
The mixer unit is, like the valve unit operation, solved in a similar manner to that of an adiabatic flash unit. In this unit, the temperature of the single outlet stream is computed for a specified outlet pressure and a duty specification of zero. The number of feed streams permitted is unlimited. The outlet product stream will *not* be split into separate phases.

Splitter

Figure 2.1.2-3: Splitter Unit



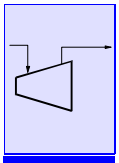
The temperature and phase of the one or more outlet streams of the splitter unit are determined by performing an adiabatic flash calculation at the specified pressure, and with duty specification of zero. The composition and phase distribution of each product stream will be identical. One feed stream or a mixture of feed streams are allowed.



2.2 Isentropic Calculations

PRO/II contains calculation methods for the following single stage constant entropy unit operations:

- Compressors (adiabatic or polytropic efficiency given)
- Expanders (adiabatic efficiency specified)



2.2.1 Compressor

General Information

PRO/II contains calculations for single stage, constant entropy (isentropic) operations such as compressors and expanders. The entropy data needed for these calculations are obtained from a number of entropy calculation methods available in PRO/II. These include the Soave-Redlich-Kwong cubic equation of state, and the Curl-Pitzer correlation method. Table 2.2.1-1 shows the thermodynamic systems which may be used to generate entropy data. User-added subroutines may also be used to generate entropy data.

Table 2.2.1-1: Thermodynamic Generators for Entropy

Generator	Phase
Curl-Pitzer[1]	VL
Lee-Kesler (LK)	VL
Lee-Kesler-Plöcker (LKP)	VL
LIBRARY	L
Soave Redlich-Kwong (SRK)	VL
Peng-Robinson (PR)	VL
SRK Kabadi-Danner (SRKKD)	VL
SRK and PR Huron-Vidal (SRKH, PRH)	VL
SRK and PR Panagiotopoulos-Reid (SRKP, PRP)	VL
SRK and PR Modified (SRKM, PRM)	VL
SRK SimSci (SRKS)	VL
UNIWAALS	VL
Benedict-Webb-Rubin-Starling (BWRS)	VL
Hexamer	VL
Hayden O'Connell (HOCV)	V
Truncated Virial (TVIRIAL)	V
Ideal-gas Dimer (IDIMER)	V

[1] The Curl-Pitzer method is used to calculate entropies for a number of thermodynamic systems. For example, by choosing the keyword SYSTEM=CS, Curl-Pitzer entropies are selected.

Once the entropy data are generated (see Section 1.2.1 of this manual, *Basic Principles*), the condition of the outlet stream from the compressor and the compressor power requirements are computed, using either a user-input adiabatic or polytropic efficiency.

Basic Calculations

For a compression process, the system pressure P is related to the volume V by:

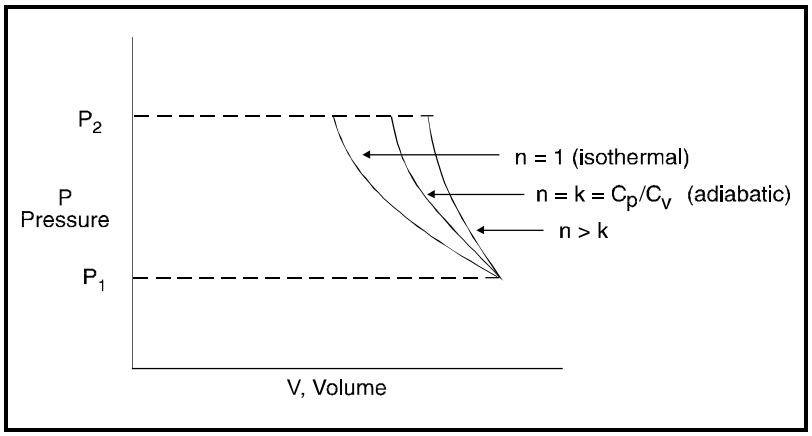
$$PV^n = Constant \quad (1)$$

where:

n = exponent

Figure 2.2.1-1 shows a series of these pressure versus volume curves as a function of n.

Figure 2.2.1-1: Polytropic Compression Curve



The curve denoted by n=1 is an isothermal compression curve. For an ideal gas undergoing adiabatic compression, n is the ratio of specific heat at constant pressure to that at constant volume, i.e.,

$$n = k = c_p / c_v \quad (2)$$

where:

k = ideal gas isentropic coefficient

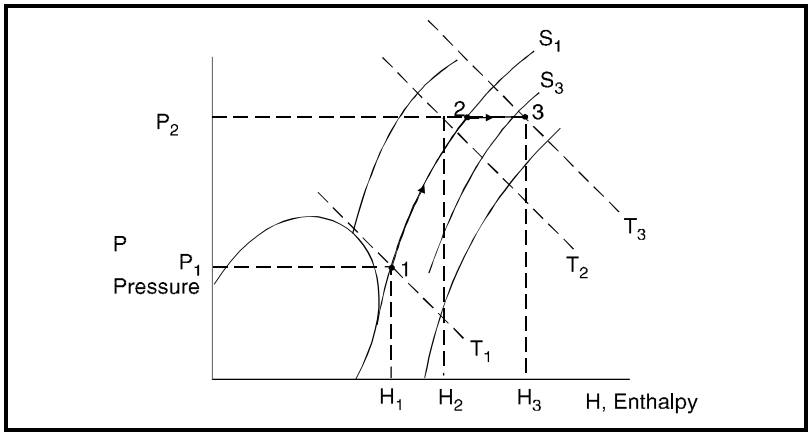
c_p = specific heat at constant pressure

c_v = specific heat at constant volume

For a real gas, n > k.

The Mollier chart (Figure 2.2.1-2) plots the pressure versus the enthalpy, as a function of entropy and temperature. This chart is used to show the methods used to calculate the outlet conditions for the compressor as follows:

Figure 2.2.1-2: Typical Mollier Chart for Compression



- A flash is performed on the inlet feed at pressure P_1, and temperature T_1, using a suitable K-value and enthalpy method, and one of the entropy calculation methods in Table 2.2.1-1. The entropy S_1, and enthalpy H_1 are obtained and the point (P_1,T_1,S_1,H_1) is obtained.
- The constant entropy line through S_1 is followed until the user-specified outlet pressure is reached. This point represents the temperature (T_2) and enthalpy conditions (H_2) for an adiabatic efficiency of 100%. The adiabatic enthalpy change ΔH_{ad} is given by:

$$\Delta H_{ad} = H_2 - H_1 \qquad (3)$$

- If the adiabatic efficiency, γ_{ad}, is given as a value less than 100 %, the actual enthalpy change is calculated from:

$$\Delta H_{ac} = \Delta H_{ad} / \gamma_{ad} \qquad (4)$$

- The actual outlet stream enthalpy is then calculated using:

$$H_3 = H_1 + \Delta H_{ac} \qquad (5)$$

- Point 3 on the Mollier chart, representing the outlet conditions is then obtained. The phase split of the outlet stream is obtained by performing an equilibrium flash at the outlet conditions.
- The isentropic work (W_s) performed by the compressor is computed from:

$$W_s = (H_3 - H_1)\, J = \Delta H_{ac} * J \qquad (6)$$

where:

J = mechanical equivalent of energy

In units of horsepower, the isentropic power required is:

$$GHP_{ad} = \Delta H_{ad} * 778 * F / 33000 \quad (7)$$

$$GHP_{ac} = \Delta H_{ac} * 778 * F / 33000 = GHP_{ad} / \gamma_{ad} \quad (8)$$

$$HEAD_{ad} = \Delta H_{ad} * 778 \quad (9)$$

where:

GHP = work, hP

ΔH = enthalpy change, BTU/lb

F = mass flow rate, lb/min

$HEAD_{ad}$ = Adiabatic Head, ft

The factor 33000 is used to convert from units of ft-lb/min to units of hP.

The isentropic and polytropic coefficients, polytropic efficiency, and polytropic work are calculated using one of two methods; the method from the *GPSA Engineering Data Book*, and the method from the *ASME Power Test Code 10*.

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PRO/II Note: For more information on using the COMPRESSOR unit operation, see Section 56, *Compressor*, of the *PRO/II Keyword Input Manual*.

ASME Method

This method is more rigorous than the default GPSA method, and yields better answers over a wider rage of compression ratios and feed compositions.

For a real gas, as previously noted, the isentropic volume exponent (also known as the isentropic coefficient), n_s, is not the same as the compressibility ratio, k. The ASME method distinguishes between k and n_s for a real gas. It rigorously calculates n_s, and never back-calculates it from k.

Adiabatic Efficiency Given

In this method, the isentropic coefficient n_s is calculated as:

$$n_s = \ln(P_2 / P_1) / \ln(V_1 / V_2) \quad (10)$$

where:

V_1 = volume at the inlet conditions

V_2 = volume at the outlet pressure and inlet entropy conditions

The compressor work for a real gas is calculated from equation (8), and the factor f from the following relationship:

$$W_{ac} = 144\left[n_s / n_s - 1\right] f P_1 V_1 \left\{(P_2 / P_1)^{(n_s - 1 / n_s)} - 1\right\} \quad (11)$$

The ASME factor f is usually close to 1. For a perfect gas, f is exactly equal to 1, and the isentropic coefficient n_s is equal to the compressibility factor k.

The polytropic coefficient, n, is defined by:

$$n = \ln(P_2 / P_1) / \ln(V_1 / V_3) \qquad (12)$$

where:

V_3 = volume at the outlet pressure and actual outlet enthalpy conditions

The polytropic work, i.e., the reversible work required to compress the gas in a polytropic compression process from the inlet conditions to the discharge conditions is computed using:

$$W_p = 144\,(n/n{-}1)\,f\,P_1\,V_1\left\{(P_2/P_1)^{(n-1/n)} - 1)\right\} \qquad (13)$$

where:

W_p = polytropic work

For ideal or perfect gases, the factor f is equal to 1.

The polytropic efficiency is then calculated by:

$$\gamma_p = W_s / W_p \qquad (14)$$

Note: This polytropic efficiency will not agree with the value calculated using the GPSA method which is computed using γ_p = {(n-1)/n} / {(k-1)/k}.

Polytropic Efficiency Given

A trial and error method is used to compute the adiabatic efficiency, once the polytropic efficiency is given. The following calculation path is used:

1. The isentropic coefficient, isentropic work, and factor f are computed using equations (10), (11), and (12).
2. The polytropic coefficient is calculated from equation (12).
3. An initial value of the isentropic efficiency is assumed.
4. Using the values of f and n calculated from steps 1 and 2, the polytropic work is calculated from equation (13).
5. The polytropic efficiency is calculated using equation (14).
6. If this calculated efficiency is not equal to the specified polytropic efficiency within a certain tolerance, the isentropic efficiency value is updated.
7. Steps 5 and 6 and repeated until the polytropic efficiency is equal to the specified value.

Reference

American Society of Mechanical Engineers (ASME), 1965, *Power Test Code*, **10**, 31-33.

GPSA Method

This GPSA method is the default method, and is more commonly used in the chemical process industry.

Adiabatic Efficiency Given

In this method, the adiabatic head is calculated from equations (3), (4), and (9). Once this is calculated, the isentropic coefficient k is computed by trial and error using:

$$HEAD_{ac} = \left\{ \left[(z_1 + z_2)/2 \right] RT_1 / \left[(k-1)/k \right] \right\} \left\{ (P_2/P_1)^{(k-1/k)} - 1 \right\} \quad (15)$$

where:

z_1, z_2 = compressibility factors at the inlet and outlet conditions

R = gas constant

T_1 = temperature at inlet conditions

This trial and error method of computing k produces inaccurate results when the compression ratio, (equal to P_2/P_1) becomes low. PRO/II allows the user to switch to another calculation method for k if the compression ratio falls below a certain set value.

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PRO/II Note: For more information on using the PSWITCH keyword to control the usage of the isentropic calculation equation, see Section 56, *Compressor*, of the *PRO/II Keyword Input Manual*.

If the calculated compression ratio is less than a value set by the user (defaulted to 1.15 in PRO/II), or if k does not satisfy $1.0 \le k \le 1.66667$, the isentropic coefficient, k, is calculated by trial and error based on the following:

$$T_2 = (z_1/z_2)\, T_1 \left\{ (P_2/P_1)^{(k-1)/k} \right\} \quad (16)$$

The polytropic compressor equation is given by:

$$HEAD_p = \left\{ \left[(z_1 + z_2)/2 \right] RT_1 / \left[(n-1)/n \right] \right\} \left\{ (P_2/P_1)^{(n-1/n)} - 1 \right\} \quad (17)$$

The adiabatic head is related to the polytropic head by:

$$HEAD_{ad}/\gamma_{ad} = HEAD_p/\gamma_p \quad (18)$$

The polytropic efficiency n is calculated by:

$$\gamma_p = [n/(n-1)] \;/\; [k/(k-1)] \quad (19)$$

The polytropic coefficient, n, the polytropic efficiency γ_p, and the polytropic head are determined by trial and error using equations (17), (18), and (19) above. The polytropic gas horsepower (which is reported as work in PRO/II) is then given by:

$$GHP_p = HEAD_p * F / 33000 \qquad (20)$$

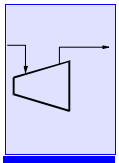
Polytropic Efficiency Given

A trial and error method is used to compute the adiabatic efficiency, once the polytropic efficiency is given. The following calculation path is used:

1. The adiabatic head is computed using equations (3), (4), and (9).
2. The isentropic coefficient, k, is determined using equations (15), or (16).
3. The polytropic coefficient, n, is then calculated from equation (19).
4. The polytropic head is then computed using equation (17).
5. The adiabatic efficiency is then obtained from equation (18).

Reference

GPSA, 1979, *Engineering Data Book*, Chapter 4, 5-9 - 5-10.



2.2.2 Expander

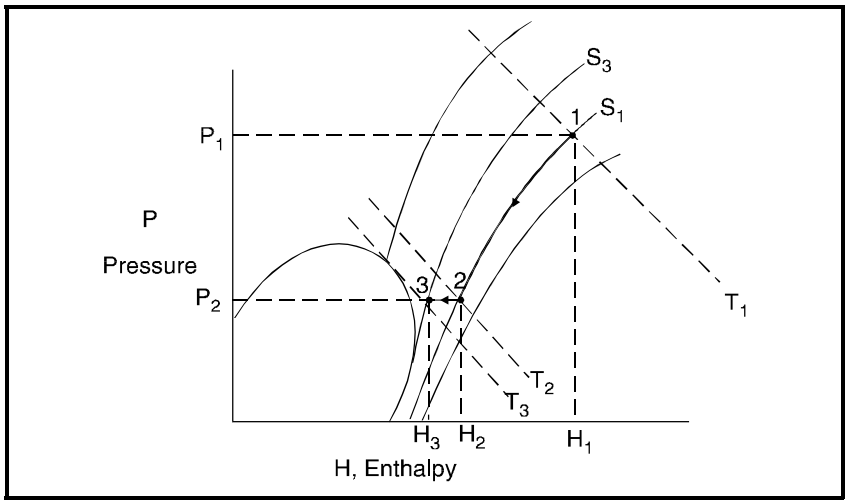
General Information

The methods used in PRO/II to model expander unit operations are similar to those described previously for compressors. The calculations however, proceed in the reverse direction to the compressor calculations.

Basic Calculations

The Mollier chart (Figure 2.2.2-1) plots the pressure versus the enthalpy, as a function of entropy and temperature. This chart is used to show the methods used to calculate the outlet conditions for the expander as follows:

Figure 2.2.2-1: Typical Mollier Chart for Expansion



- A flash is performed on the inlet feed at the higher pressure P_1, and temperature T_1, using a suitable K-value and enthalpy method, and a suitable entropy calculation methods. The entropy S_1, and enthalpy H_1 are obtained and the point (P_1,T_1,S_1,H_1) is obtained.
- The constant entropy line through S_1 is followed until the lower user-specified outlet pressure is reached. This point represents the temperature (T_2) and enthalpy conditions (H_2) for an adiabatic expander efficiency of 100%. The adiabatic enthalpy change ΔH_{ad} is given by:

$$\Delta H_{ad} = H_2 - H_1 \qquad (1)$$

- If the adiabatic efficiency, γ_{ad}, is given as a value less than 100 %, the actual enthalpy change is calculated from:

$$\Delta H_{ac} = \Delta H_{ad} / \gamma_{ad} \qquad (2)$$

- The actual outlet stream enthalpy is then calculated using:

$$H_3 = H_1 + \Delta H_{ac} \tag{3}$$

- Point 3 on the Mollier chart, representing the outlet conditions, is then obtained. The phase split of the outlet stream is obtained by performing an equilibrium flash at the outlet conditions.
- The isentropic expander work (W_s) is computed from:

$$W_s = (H_3 - H_1)\, J = \Delta H_{ac} * J \tag{4}$$

where:

J = mechanical equivalent of energy

In units of horsepower, the isentropic expander power output is:

$$GHP_{ac} = \Delta H_{ad} * 778 * F / 33000 \tag{7}$$

$$GHP_{ac} = \Delta H_{ac} * 778 * F / 33000 = GHP_{ad} / \gamma_{ad} \tag{8}$$

$$HEAD_{ad} = \Delta H_{ad} * 778 \tag{9}$$

where:

GHP = work, hP

ΔH = enthalpy change, BTU/lb

F = mass flow rate, lb/min

$HEAD_{ad}$ = Adiabatic Head, ft

The factor 33000 is used to convert from units of ft-lb/min to units of hP.

Adiabatic Efficiency Given

If an adiabatic efficiency other than 100 % is given, the adiabatic head is calculated from equations (3), (4), and (9). Once this is calculated, the isentropic coefficient k is computed by trial and error using:

$$HEAD_{ac} = \left\{\left[(z_1 + z_2)/2\right] RT_1 / \left\{(k-1)/k\right\}\right\} \left\{(P_2/P_1)^{(k-1/k)} - 1\right\} \tag{10}$$

where

z_1, z_2 = compressibility factors at the inlet and outlet conditions

R = gas constant

T_1 = temperature at inlet conditions

The polytropic expander equation is given by:

$$HEAD_p = \left\{\left[(z_1 + z_2)/2\right] RT_1 / \left\{(n-1)/n\right\}\right\} \left\{(P_2/P_1)^{(n-1/n)} - 1\right\} \tag{11}$$

The adiabatic head is related to the polytropic head by:

$$HEAD_{ad} / \gamma_{ad} = HEAD_p / \gamma_p \quad (12)$$

The polytropic efficiency n is calculated by:

$$\gamma_p = [n / (n-1)] / [k / (k-1)] \quad (13)$$

The polytropic coefficient, n, the polytropic efficiency γ_p, and the polytropic head are determined by trial and error using equations (11), (12), and (13) above. The polytropic gas horsepower output by the expander (which is reported as work in PRO/II) is then given by:

$$GHP_p = HEAD_p * F / 33000 \quad (14)$$

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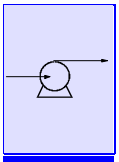
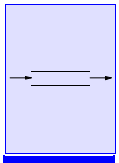


2.3 Pressure Calculations

PRO/II contains pressure calculation methods for the following units:

- Pipes (single and two-phase flows)
- Pumps (incompressible fluids)



2.3.1 *Pipes*

General Information

PRO/II contains calculations for single liquid or gas phase or mixed phase pressure drops in pipes. The PIPE unit operation uses transport properties such as vapor and/or liquid densities for single-phase flow, and surface tension for vapor-liquid flow. The transport property data needed for these calculations are obtained from a number of transport calculation methods available in PRO/II. These include the PURE and PETRO methods for viscosities. Table 2.3.1-1 shows the thermodynamic methods which may be used to generate viscosity and surface tension data.

Table 2.3.1-1: Thermodynamic Generators for Viscosity and Surface Tension

Viscosity	Surface Tension
PURE (V & L)	PURE
PETRO (V & L)	PETRO
TRAPP (V & L)	
API (L)	
SIMSCI (L)	
KVIS (L)	

PRO/II contains numerous pressure drop correlation methods, and also allows for the input of user-defined correlations by means of a user-added subroutine.

Basic Calculations

An energy balance taken around a steady-state single-phase fluid flow system results in a pressure drop equation of the form:

$$\underset{\textbf{\textit{total}}}{(dP/dL)_t} = \underset{\textbf{\textit{friction}}}{(dP/dL)_f} + \underset{\textbf{\textit{elevation}}}{(dP/dL)_e} + \underset{\textbf{\textit{acceleration}}}{(dP/dL)_{acc}} \qquad (1)$$

The pressure drop consists of a sum of three terms:

- the reversible conversion of pressure energy into a change in elevation of the fluid,
- the reversible conversion of pressure energy into a change in fluid acceleration, and
- the irreversible conversion of pressure energy into friction loss.

The individual pressure terms are given by:

$$(dP/dL)_f = f\rho v^2 / 2g_c d \quad (2)$$

$$(dL/dL)_e = g\rho\sin\phi / g_c \quad (3)$$

$$(dP/dL)_{acc} = \rho v / g_c \, dv/dL \quad (4)$$

where:

l and g refer to the liquid and gas phases

P = the pressure in the pipe

L = the total length of the pipe

d = the diameter of the pipe

f = friction factor

ρ = fluid density

v = fluid velocity

g_c = acceleration due to standard earth gravity

g = acceleration due to gravity

ϕ = angle of inclination

$(dP/dL)_t$ = total pressure gradient

$(dP/dL)_f$ = friction pressure gradient

$(dP/dL)_e$ = elevation pressure gradient

$(dP/dL)_{acc}$ = acceleration pressure gradient

For two-phase flow, the density, velocity, and friction factor are often different in each phase. If the gas and liquid phases move at the same velocity, then the ‘‘no slip’’ condition applies. Generally, however, the no-slip condition will not hold, and the mixture velocity, v_m, is computed from the sum of the phase superficial velocities:

$$v_m = v_{sl} + v_{gl} \quad (5)$$

where:

v_{sl} = superficial liquid velocity = volumetric liquid flowrate/cross sectional area of pipe

v_{gl} = superficial gas velocity = volumetric gas flowrate/cross sectional area of pipe

Equations (2), (3), and (4) are therefore rewritten to account for these phase property differences:

$$(dP/dL)_f = f_{tp}\,\rho_{tp}\,v_{tp}^2 / 2g_c\,d \quad (6)$$

$$(dP/dL)_e = g\rho_{tp}\sin\phi / g_c \quad (7)$$

$$(dP/dL)_{acc} = \rho_{tp}\,v_{tp}/g_c\,(dv_{tp}/dL) \quad (8)$$

where:

ρ_{tp} = fluid density = $\rho_l H_L + \rho_g H_g$

H_L, H_g = liquid and gas holdup terms subscript *tp* refers to the two-phases

Pressure Drop Correlations

The hybrid pressure drop methods available in PRO/II each uses a separate method to compute each contributing term in the total pressure drop equation (1). These methods are described below.

Beggs-Brill-Moody (BBM)

This method is the default method used by PRO/II, and is the recommended method for most systems, especially single-phase systems. For the pressure drop elevation term, the friction factor, f, is computed from the relationship:

$$f / f_n = f_{tp} / f_n = \exp(s) \quad (9)$$

The exponent s is given by:

$$s = y / (-0.0523 + 3.182y - 0.8725y^2 + 0.01853y^4) \quad (10)$$

$$s = \ln(2.2e^y - 1.2), \quad 1 < e^y < 1.2 \quad (11)$$

$$y = \ln(\lambda_L / H_L^2) \quad (12)$$

where:

f_n = friction factor obtained from the Moody diagram for a smooth pipe

λ_L = no-slip liquid holdup = $v_{sl} / (v_{sl} + v_{sg})$

v_{sl} = superficial liquid velocity

v_{sg} = superficial gas velocity

The liquid holdup term, H_L, is computed using the following correlations:

$$H_{L0} = (a\lambda_L^b / N_{Fr}^c) \quad (13)$$

$$H_L = H_{L0}, \quad \text{when } \phi = 0$$

$$H_L = H_{L0}\,\Psi, \quad \text{when } \phi \neq 0$$

$$\Psi = 1 + (1 - \lambda_L)\ln\left(d\lambda_L^e N_{Lv}^f N_{Fr}^g\right)\left\{\sin(1.8\phi) - 0.333\sin^3(1.8\phi)\right\} \quad (14)$$

where:

N_{Fr} = Froude number

N_{Lv} = liquid velocity number

a,b,c,d,e,f,g = constants

The BBM method calculates the elevation and acceleration pressure drop terms using the relationships given in equations (3) and (4) (or equations (7) and (8) for two-phase flow).

Beggs-Brill-Moody-Palmer (BBP)

This method uses the same elevation, and acceleration correlations described above for the Beggs-Brill-Moody (BBM) method. The equation for the friction pressure drop term is the same as that given for the BBM method in equations (9) through (12). For this method, however, the Palmer corection factors given below are used to calculate the liquid holdup.

$$H_L = 0.541\, H_{L,BBM,}\ \phi < 0$$

$$H_L = 0.918\, H_{L,BBM},\ \phi > 0 \qquad (15)$$

where:

$H_{L,BBM}$ = liquid holdup calculated using the BBM method

Dukler-Eaton-Flanigan (DEF)

This method uses the Dukler correlation to calculate the friction term. The friction factor is given by:

$$f/f_n = 1 + y/\left(1.281 - 0.478y + 0.444y^2 - 0.094y^3 + 0.0084y^4\right) \qquad (16)$$

$$y = -\ln(\lambda_L) \qquad (17)$$

$$f_n = 0.0056 + 0.5N_{Re} \qquad (18)$$

where:

N_{Re} = Reynolds number

The liquid holdup, H_L, used in calculating the mixture density, ρ, in the friction term is computed using the Eaton correlation. In this correlation, the holdup is defined as a function of several dimensionless numbers.

The elevation term is calculated using equation (3). The mixed density, ρ, however, is calculated not by using the Eaton holdup, but by using the liquid holdup calculated by the Flanigan correlation:

$$H_L = 1/\left(1 + 0.326\, v_{sg}^{1.06}\right) \qquad (19)$$

The acceleration term is calculated using the Eaton correlation:

$$(dP/dL)_{acc} = W_1\left(\Delta v_1\right)^2 + W_g\left(\Delta v_g\right)^2 / \left(2g_c\, q_m\, \Delta L\right) \qquad (20)$$

where:

W = mass flow rate

v = fluid velocity

v_{sg} = superficial gas velocity

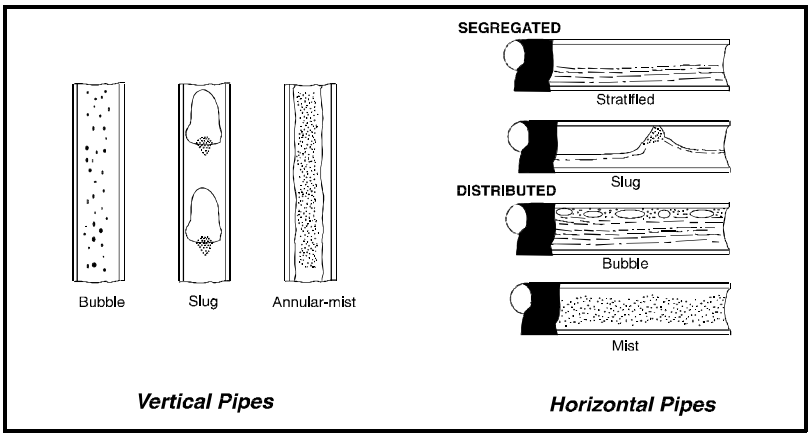
q_m = mixture flow rate

subscripts g and l refer to the gas and liquid phases

Mukherjee-Brill (MB)

The Mukherjee-Brill method is recommended for gas condensate systems. In the MBN method, a separate friction pressure drop term is given for each region of flow. Figure 2.3.1-1 shows the various flow patterns which the MB method is able to handle.

Figure 2.3.1-1: Various Two-phase Flow Regimes



For stratified flows in horizontal pipes:

$$(dp/dL)_f = f\rho_g\, v_g^2 / 2g_c\, d \qquad (21)$$

For bubble or slug flows:

$$(dP/dL)_f = f\rho_m\, v_m^2 / 2g_c\, d \qquad (22)$$

For mist flows:

$$(dP/dL)_f = ff_{fr}\, \rho_g\, v_g^2 / 2g_c\, d \qquad (23)$$

where:

f_{fr} = factor calculated from a correlation

For bubble, slug, and mist flows, the elevation pressure drop is computed using equation (7), but for stratified flows, the fluid density used is the gas phase density.

The acceleration pressure drop term is given by:

$$(dP/dL)_{acc} = \left(v_m \, v_s^g \, g \, \rho_{tp} / g_c \, P\right)(dP/dL)_t \qquad (24)$$

where:

v_s = slip velocity

The density, ρ_{tp}, is equal to the gas density for stratified flows only.

A separate expression is used to calculate the holdup for each flow pattern. These are given as:

ϕ < 0 Bubble, Slug, Mist flow

$$H_L = e^{H_2}, H_2 = H_1\left(\frac{N_{GV}^{0.371771}}{N_{LV}^{0.393962}}\right) \qquad (25)$$

$$H_1 = -0.51664 + 0.789805 \sin\phi + 0.551627 \sin^2\phi + 15.519214 \, N_L^2 \qquad (26)$$

ϕ < 0 Stratified flow

$$H_L = e^{H_2}, H_2 = H_1\left(\frac{N_{GV}^{0.079961}}{N_{LV}^{0.604887}}\right) \qquad (27)$$

$$H_1 = -1.330282 + 4.808139 \sin\phi + 4.171584 \sin^2\phi + 56.262268 \, N_L^2 \qquad (28)$$

$\phi \geq$ 0 (all flow patterns)

$$H_L = e^{H_2}, H_2 = H_1\left(\frac{N_{GV}^{0.475686}}{N_{LV}^{0.288657}}\right) \qquad (29)$$

$$H_1 = -0.380113 + 0.129875 \sin\phi - 0.119788 \sin^2\phi + 2.343227 \, N_L^2 \qquad (30)$$

where:

N_L = liquid viscosity number

Gray

The Gray method has been especially developed for gas condensate wells, and should not be used for horizontal piping. The recommended ranges for use are:

- Angle of inclination, ϕ = ≥ 70 degrees
- Velocity, v < 50 ft/s,
- Pipe diameter, d < 3.5 inches
- Liquid condensate loading ~ 50 bbl/MMSCF

The friction pressure drop term is computed from equations (2) or (6), where the friction factor used is obtained from the Moody charts. The elevation term is calculated using equations (3) or (7), while the acceleration term is given by equation (24).

The liquid holdup term, H_L is given by:

$$H_L = 1 - H_g \tag{31}$$

$$H_g = \frac{1 - e^{A^1}}{R + 1} \tag{32}$$

$$A^1 = -2.314 \left[N_v \left(1 + \frac{205}{N_C} \right) \right]^{B^1} \tag{33}$$

$$B^1 = 0.0814 \left[1 - 0.05554 \ln \left(1 + \frac{0.730R}{R + 1} \right) \right] \tag{34}$$

$$R = \frac{V_{sL}}{V_{sg}} \tag{35}$$

$$N_v = \frac{\rho_m^2 v_{sm}^2}{g \sigma_L (\rho_L - \rho_g)} \tag{36}$$

$$N_D = \frac{g (\rho_l - \rho_g) D^2}{\sigma_L} \tag{37}$$

$$\sigma_L = \frac{\sigma_0 q_0 + 0.617 \sigma_w q_w}{q_0 + 0.617 q_w} \tag{38}$$

where:

σ = surface tension

q_o = *in situ* oil volumetric flowrate

q_w = *in situ* water volumetric flowrate

q_m = mixture volumetric flowrate

N_D = diameter number

l (or *L)* and *g* (or *G)* refer to the liquid and gaseous phases

Oliemens

This method uses the Eaton correlation previously described above to calculate the liquid holdup. The friction factor is obtained from the Moody diagrams, and the friction pressure term is computed using:

$$(dP/dL)_f = fG^2 / \left(2\, g_c\, d_{eff} \rho_{OLI} 144\right) \quad (39)$$

$$G = q_1\rho_1 + q_g\rho_g / (1 - B_L)\, A \quad (40)$$

$$\rho_{OLI} = \rho_{tp} / (1 - B_L) \quad (41)$$

$$B_L = H_L - H_{Lns} \quad (42)$$

where:

G = mass flux

H_{Lns} = no-slip liquid holdup

ρ_{OLI} = Oliemens density

d_{eff} = effective diameter

A = pipe cross sectional area

ρ_{tp} = fluid density = $\rho_l H_L + \rho_g H_g$

l (or L) and g (or G) refer to the liquid and gas phases respectively

The acceleration term is set equal to zero, while the elevation pressure drop term is computed using:

$$(dP/dL)_e = \rho_s\, g \sin\phi / g_c\, 144 \quad (43)$$

$$\rho_s = \rho_1 H_L + \rho_g H_g,\ \phi > 0$$

$$\rho_s = \rho_g,\ \phi > 0 \text{ and } H_L < 1.0$$

$$\rho_s = \rho_1,\ \phi < 0 \text{ and } H_L = 1 \quad (44)$$

where:

ϕ = angle of inclination

subscripts l (or L) and g (or G) refer to the liquid and gas phases respectively

Hagedorn-Brown (HB)

This method is recommended for vertical liquid pipelines, and should not be used for horizontal pipes. The liquid holdup term is calculated from a correlation of the form:

$$H_L = \textit{function of}\left(N_{lV}, N_{GV}, N_D\right) \quad (45)$$

where:

N_{lV}, N_{GV}, N_D are the dimensionless liquid velocity number, gas velocity number, and diameter number.

The friction factor is obtained from the Moody diagrams, and the friction pressure term is computed using equations (2) or (6), depending on whether there is single- or two-phase flow.

58

PRO/II Note: For more information on using these pressure drop correlation methods in the PIPE unit operation, see Section 58, *Pipe*, of the *PRO/II Keyword Input Manual*.

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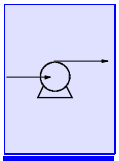

2.3.2 Pumps

General Information

The PUMP unit operation in PRO/II contains methods to calculate the pressure and temperature changes resulting from pumping an incompressible fluid.

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PRO/II Note: For more information on using the PUMP unit operation, see Section 52, *Pump*, of the *PRO/II Keyword Input Manual.*

Basic Calculations

The GPSA pump equation is used to relate the horsepower required by the pump to the fluid pressure increase:

$$HP = q\,\Delta P\,/\,(1714.3\,e) \qquad (1)$$

where:

HP = required pump power, hp

q = volumetric flow rate, gal/min.

ΔP = pressure increase, psi

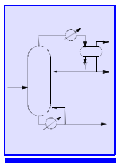
e = percent efficiency

The factor 1714.3 converts the pump work to units of horsepower. The work done on the fluid calculated from (1) above is added to the inlet enthalpy. The temperature of the outlet fluid is then obtained by performing an adiabatic flash.

Note: The PUMP unit should only be used for incompressible fluids. Compressible fluids may be handled using the COMPRESSOR unit operation.

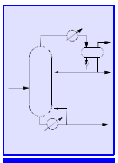
Reference

GPSA Engineering Data Book, 9th Ed., 5-9



2.4 Distillation and Liquid-Liquid Extraction Columns

The PRO/II simulation program is able to model rigorous and shortcut distillation columns, trayed and packed distillation columns (random and structured packings), as well as liquid-liquid extraction columns.



2.4.1 Rigorous Distillation Algorithms

General Information

This chapter presents the equations and methodology used in the solution of the distillation models found in PRO/II. It is recommended reading for those who want a better understanding of how the distillation models are solved. This chapter also explains how the intermediate printout relates to the equations being solved.

All of the distillation algorithms in PRO/II are rigorous equilibrium stage models. Each model solves the heat and material balances and vapor-liquid equilibrium equations. The features available include pumparounds, five condenser types, generalized specifications, and interactions with flowsheeting unit operations such as the Controller and Optimizer. Reactive distillation is available for distillation and liquid-extraction. Automatic water decant is available for water/hydrocarbon systems.

Modelling a distillation column requires solving the heat and material balance equations and the phase equilibrium equations. PRO/II offers four different algorithms for modeling of distillation columns:

- the Inside/Out (I/O) algorithm,
- the Sure algorithm,
- the Chemdist algorithm, and
- the ELDIST algorithm.

For electrolyte systems the Eldist algorithm is available, and for liquid- liquid extractors the LLEX algorithm should be used. Eldist, Chemdist and the LLEX also allow chemical reaction. Eldist is used when equilibrium electrolytic reactions are present. Chemdist and LLEX allow kinetic, equilibrium (non-electrolyte) and conversion reactions to occur on one or more stages.

For most systems, SimSci recommends using the I/O algorithm. When more than one algorithm can be used to solve a problem, the I/O algorithm will usually converge the fastest. The I/O algorithm can be used to solve most refinery problems, and is very fast for solving crude columns and main fractionators. The I/O algorithm also solves many chemical systems, and when possible should be the first choice for systems with a single liquid phase.

The Sure algorithm in PRO/II is the same time proven algorithm as in PROCESS. This algorithm is particularly useful for hydrocarbon systems where water is present. It is the best algorithm to solve ethylene quench towers which have large water decants in the upper portion of the tower. The Sure algorithm is also appropriate for many other refining and chemical systems.

Chemdist is a new algorithm developed at SimSci for the simulation of highly non-ideal chemical systems. Chemdist is a full Newton-Raphson method, with complete analytic derivatives. This includes composition derivatives for activity and fugacity coefficients. Chemdist allows two liquid phases to form on any stage in the column, and also supports a wide range of two liquid phase condenser configurations. Chemdist with chemical reactions allows In-Line Procedures for non-power law kinetic reactions.

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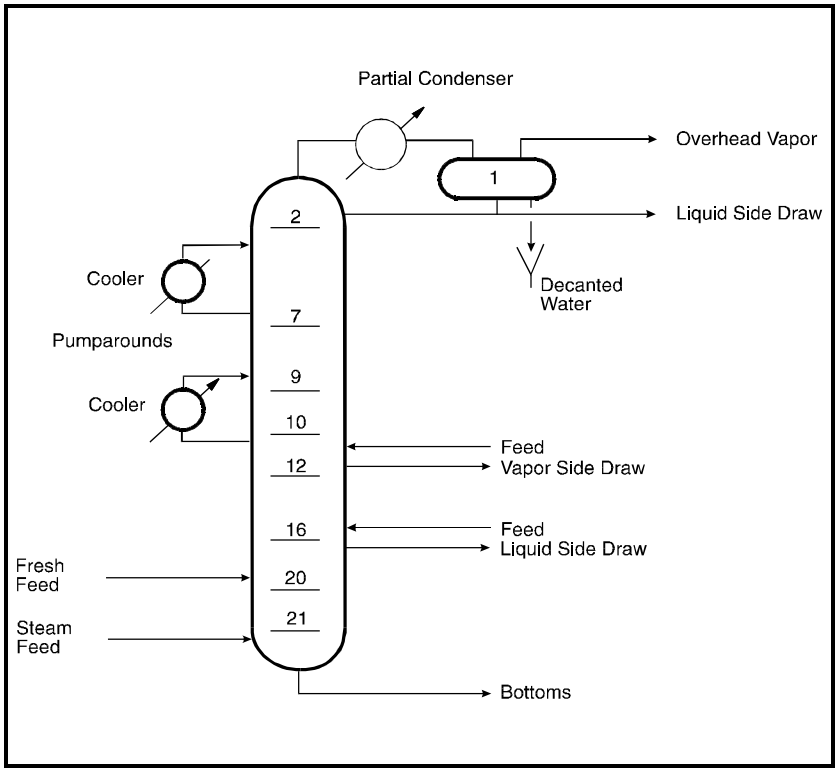
PRO/II Note: For more information on inputting reaction kinetics using In-Line Procedures, see Section 47, *Procedure Data*, of the *PRO/II Keyword Input Manual*.

Eldist is an extension of Chemdist for modeling distillation of aqueous electrolyte mixtures. The aqueous chemistry is solved using third party software from OLI Systems. The electrolyte calculation computes true vapor-liquid equilibrium K-values, which are converted to apparent vapor-liquid equilibrium K-Values. Eldist then uses these in the vapor-liquid equilibrium calculations.

General Column Model

A schematic diagram of a complex distillation column is shown in Figure 2.4.1-1. A typical distillation column may have multiple feeds and side draws, a reboiler, a condenser, pumparounds, and heater-coolers. The column configuration is completely defined; the number of trays and the locations of all feeds, draws, pumparounds and heater-coolers. Note that the optimizer can change feed, draw and heater-cooler locations.

Figure 2.4.1-1: Schematic of Complex Distillation Column



Trays are numbered from the top down. The condenser and reboiler are treated as theoretical stages, and when present the condenser is stage one.

There are no ‘‘hard limits’’ on the number of feeds, draws, pumparounds etc. This results from the PRO/II memory management system.

Table 2.4.1-1 shows the features available with each algorithm. Pumparounds can be used for liquid and/or vapor. The return tray can be above or below the draw tray. Note that when the pumparound return is mixed phase (liquid and vapor) that both the vapor and the liquid are returned to the same tray.

PRO/II provides hydrodynamic calculations for packings supplied by Norton Co. and Sulzer Brothers. Both rating and design calculations are available. In rating mode, the diameter and height of packing are specified and the pressure drop across the packed section is determined. In design mode, the height of packing and the pressure drop are specified, and the packing diameter is calculated.

Tray rating and sizing is also available and may be performed for new and existing columns with valve, sieve and bubble cap trays. Valve tray calculations are done using the methods from Glitsch. Tray hydraulics for sieve trays are calculated using the methods of Fair and for bubble cap trays with the methods of Bolles. Rating and design calculations are available.

The I/O and Sure algorithms provide a free water decant option. This is used in refinery applications to model water being decanted at the condenser or at other stages in the distillation column.

Table 2.4.1-1: Features Overview for Each Algorithm

	I/O	Sure	Chemdist	LLEX	Eldist
Pumparounds	Y	Y	N	N	N
Packed Column	Y	Y	Y	N	Y
Tray Rating/Sizing	Y	Y	Y	N	Y
Two Liquids on any tray	N	Y	Y	—	N
Free Water Decant	Y	Y	N	—	N
Tray Efficiency	Y	N	Y(2)	N	Y(2)
Solids	Y	Y	Y	N	(1)
LS Components	N	N	N	N	Y
Electrolytes	N	N	N	N	Y
Kinetic Reaction	N	N	Y	Y	N
Equilibrium Reaction	N	N	Y	Y	N
Conversion Reaction	N	N	Y	Y	N

(1) Eldist predicts solids precipitation on stages, but does not allow solid formation for mass balance purposes.

(2) Only vaporization efficiencies available.

Side draws may be either liquid or vapor, and the location and phase of each must be specified. Solid side draws are not allowed. There may be an unlimited number of products from each stage.

Feed tray locations are given as the tray number upon which the feed is introduced. A feed may be liquid, vapor or mixed phase. PRO/II also allows for different conventions for mixed phase (vapor/liquid) feeds. The default convention NOTSEPARATE introduces both the liquid and the vapor to the same stage. SEPARATE places the liquid portion of the feed on the designated feed tray and the vapor portion of the feed on the tray above the designated feed tray.

A pumparound is defined as a liquid or vapor stream from one tray to another. The return tray can be either above or below the pumparound draw tray. The pumparound flowrate can be specified or calculated to satisfy a process requirement. If a heater/cooler is used with the pumparound, it must be located on the pumparound return tray. The pumparound return temperature, pressure, liquid fraction, and temperature drop will be computed if it is not specified.

Heater/coolers may be located on any tray in the column. A heater/cooler is treated only as a heat source or sink. Rigorous models of external heat exchangers are available via the attached heat exchanger option.

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PRO/II Note: For more information on using attached heat exchangers, see Section 81, *Simple Heat Exchanger*, of the *PRO/II Keyword Input Manual*.

Feed rates, side draw rates and heater/cooler duties may be either fixed or computed. For each varied rate or duty, a corresponding design specification must be made.

Mathematical Models

There are many different approaches to solving the distillation equations. This is evident from the large number of articles on the subject in the chemical engineering literature. There are many classes of distillation problems; wide and narrow boiling, azeotropic, homogeneous and heterogeneous liquid phases, electrolytic and reactive. Unfortunately, no one algorithm is yet available which can reliably solve all of these problems. PRO/II provides different algorithms which excel in solving certain classes of problems and often provide solution capability over a very wide range of problems. Eldist is designed to solve a specific class of problems, namely electrolytic systems. The LLEX (liquid-liquid extractor) is for liquid liquid extraction systems.

Inside Out Algorithm

The Inside/Out (I/O) column algorithm in PRO/II is based on an article by Russell in 1983. The I/O column algorithm contains a number of novel features which contribute to its excellent convergence characteristics. The algorithm is partitioned into an inner and outer loop. In the inner loop, the heat, material and design specifications are solved. Simple thermodynamic models for enthalpy and vapor liquid equilibrium (VLE) K-values are used in the inner loop. This, along with the form of the simple model and the choice of primitive variables, allows the inner loop to be solved quickly and reliably. In the outer loop, the simple thermodynamic model parameters are updated based on the new compositions and the results of rigorous thermodynamic calculations. When the rigorously computed enthalpies and K-values match those of the simple thermodynamic models, and the design specifications are met, the algorithm is solved.

Inner Loop

The primitive variables in the inner loop are the stripping factors and sidestream withdrawal factors. The inner loop equations are the stage enthalpy balances and the design specifications. The stripping factor here is defined as:

$$S_j = \left(\frac{K_b V}{L}\right)_j \tag{1}$$

where:

S_j = the Stripping Factor for stage j

V = the net vapor leaving the stage

L = the net liquid leaving the stage

K_b = the base component K-value from the simple K-value model (see equation (11))

The inner loop solves the system of equations:

$$H_1 = f\left(S_1, S_2, ..., S_n, \left(\frac{LSS}{L}\right)_k\right) = 0$$

$$H_2 = f\left(S_1, S_2, ..., S_n, \left(\frac{LSS}{L}\right)_k\right) = 0$$

.

.

.

$$H_n = f\left(S_1, S_2, ..., S_n, \left(\frac{LSS}{L}\right)_k\right) = 0$$

$$SP_k = f\left(S_1, S_2, ..., S_n, \left(\frac{LSS}{L}\right)_k\right) = 0 \tag{2}$$

In equation (2) H_j is the heat balance for stage j:

$$H_j = H_j^L L_j \left(1 + \left(\frac{LSS}{L}\right)_j\right) + H_j^V V_j \left(1 + \left(\frac{VSS}{V}\right)_j\right) - H_{j-1}^L L_{j-1} - H_{j+1}^V V_{j+1}$$

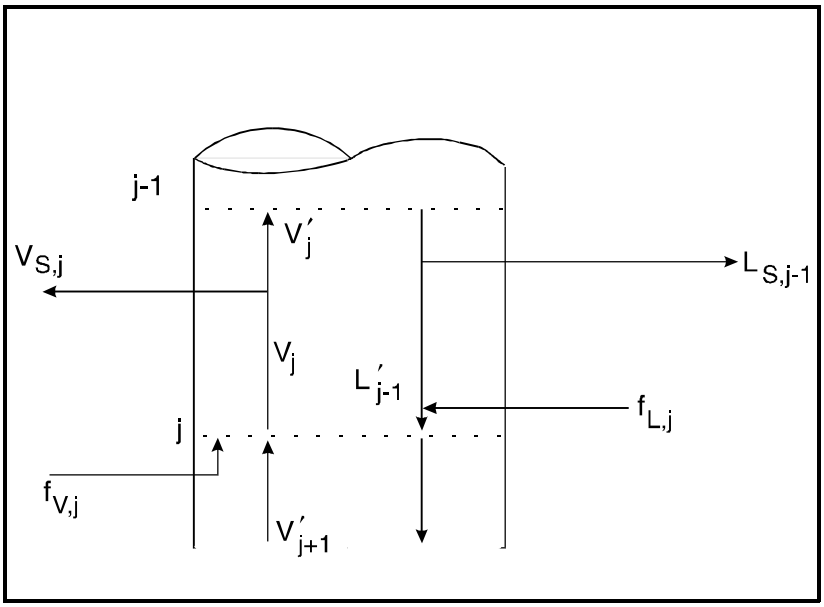
$$- \sum_{i=1}^{NF} H_i^F F_i - \sum_{i=1}^{NQ} Q_i = 0 \qquad (3)$$

and SP_k is a design specification equation.

This system of equations is solved using the Newton-Raphson method. The first Jacobian matrix is obtained by finite difference approximation. This Jacobian is then inverted, and at subsequent iterations the inverse Jacobian is updated using Broyden's method.

To evaluate the errors in the enthalpy and specification equations for a given set of stripping factors, the component flows and stage temperatures must be computed for the given stripping factors and simple model parameters. Figure 2.4.1-2 shows a schematic diagram of a simple stage.

Figure 2.4.1-2: Schematic of a Simple Stage for I/O



Writing the material balance for this stage in terms of net liquid and vapor flowrates results in:

$$f_j = -l_{j-1} + l_j \left[1 + \left(\frac{LSS}{L_j}\right)_j\right] + v_j \left[1 + \left(\frac{VSS}{V_j}\right)_j\right] - v_{j+1} \qquad (4)$$

where:

l = the component liquid rate, moles/time

v = the component vapor rate, moles/time

f = the component feed rate, moles/time

Given the equilibrium relationship $y_{i,j} = K_{i,j}\, x_{i,j}$ it is possible to remove v from equation (4). This is done as follows:

$$v_{i,j} = y_{i,j} v_j = K_{i,j}\, x_{i,j}\, v_j = \frac{K_{i,j}\, v_j\, l_{i,j}}{L_j} \tag{5}$$

where K is the vapor liquid equilibrium fugacity ratio. Now the component mass balance can be written as:

$$f_j = -l_{i,j-1} + l_{i,j}\left\{\left[1+\left(\frac{LSS}{L}\right)_j\right]+\left[\frac{K_{i,j}\, V_j}{L_j}\right]\left[1+\left(\frac{VSS}{V}\right)_j\right]\right\} - l_{i,j}\left(\frac{K_{i,j+1}\, V_{j+1}}{L_{j+1}}\right) \tag{6}$$

If K is assumed constant, equation (5) results in a linear system of equations for component i which form a tridiagonal system:

$$\begin{bmatrix} B_{i,1} & C_{i,1} & & & & & \\ -1 & B_{i,2} & C_{i,2} & & & & \\ & -1 & B_{i,3} & C_{i,3} & & & \\ & & \cdot & & \cdot & & \\ & & & & \cdot & & \\ & & & & -1 & B_{i,j-1} & C_{i,n-1} \\ & & & & & -1 & B_{i,n} \end{bmatrix} \begin{bmatrix} l_{i,1} \\ l_{i,2} \\ l_{i,3} \\ \cdot \\ \cdot \\ \cdot \\ l_{i,n-1} \\ l_{i,n} \end{bmatrix} \begin{bmatrix} f_{i,1} \\ f_{i,2} \\ f_{i,3} \\ \cdot \\ \cdot \\ \cdot \\ f_{i,n-1} \\ f_{i,n} \end{bmatrix} \tag{7}$$

where B and C are given by:

$$B_{i,j} = \left[1+\left(\frac{LSS}{L}\right)_j\right]+\left[\frac{K_{i,j}\, V_j}{L_j}\right]\left[1+\left(\frac{VSS}{V}\right)_j\right] \tag{8}$$

$$C_{i,j} = -\left(\frac{K_{i,j+1}\, V_{j+1}}{L_{j+1}}\right) \tag{9}$$

Sidestream withdrawal factors are defined as:

$$R_{Lj} = 1+\left(\frac{LSS}{L}\right)_j$$

$$R_{Vj} = 1+\left(\frac{VSS}{V}\right)_j \tag{10}$$

The vapor equilibrium K-value simple model is given by:

$$K_{i,j} = \alpha_{ij}\, K_b \tag{11}$$

where $\alpha_{i,j}$ is the relative volatility for component i on stage j and K_b is the base component K-value modeled by:

$$\ln(K_b) = A + B\left(\frac{1}{T} - \frac{1}{T^{ref}}\right) \tag{12}$$

In equation (12) T^{ref} is a reference temperature. Using this definition of the simple K-value model and the sidestream withdrawal factors, the material balance (4) can be rewritten as:

$$f_{i,j} = -l_{i,j-1} + l_{i,j}\,(R_{L,j} + a_{i,j}\,S_j R_{V,j}) - l_{i,j+1}\,(a_{i,j+1}\,S_{j+1}) \qquad (13)$$

The set of equations defined by (13) still form a tridiagonal matrix so that equation (7) still applies. B_{ij} and C_{ij} from (8) and (9) now become:

$$B_{i,j} = R_{L,j} + \alpha_{i,j} S_j R_{Vj}$$

$$C_{i,j} = -\alpha_{i,j+1}\,S_{j+1} \qquad (14)$$

Outer Loop

The outer loop in the Inside/Out algorithm updates the simple thermodynamic model parameters and checks for convergence. In the inner loop, the distillation equations are solved for the current simple thermodynamic models. The convergence check in the outer loop therefore compares the rigorously computed enthalpies and VLE K-values from the new compositions resulting from the inner loop calculations.

The simple model used for VLE K-values is given by equations (11) and (12). The initial value of K_b on each stage j is computed by:

$$\ln(K_b) = \sum_i w_i \ln(K_i)$$

$$w_i = \frac{t_i}{\sum_i t_i}$$

$$t_i = y_i \frac{\delta(\ln K_i)}{\delta\left(\frac{1}{T}\right)} \qquad (15)$$

The simple K-values can be calculated very quickly for a given temperature. Also, once new molar flows are computed in the inner loop, a new bubble point temperature can be easily computed. Once the molar flows are computed, the mole fractions are obtained from:

$$x_{i,j} = \frac{l_{i,j}}{\sum_i l_{i,j}} \qquad (16)$$

and substituting equation (11) into the bubble point equation:

$$\sum_i y_{i,j} = \sum_i K_{i,j}\,x_{i,j} = 1 \qquad (17)$$

$$K_b = \frac{1}{\sum_i \alpha_i x_i} \qquad (18)$$

Once K_b has been determined, equation (12) can be arranged so that the bubble point temperature can be solved for directly. The bubble point expression is:

$$T^{bubble} = \left[\frac{\ln(K_b - A)}{B} + \frac{1}{T^{ref}} \right]^{-1} \quad (19)$$

The simple enthalpy models are of the form:

$$H_v = H_v^0 - \Delta H_v$$

$$H_L = H_L^0 - \Delta H_L \quad (20)$$

where:

H_v = the vapor enthalpy

H_L = the liquid enthalpy

H_v^0 = the vapor ideal gas enthalpy

H_L^0 = the liquid ideal gas enthalpy

ΔH_v = the vapor enthalpy departure from the ideal gas enthalpy

ΔH_L = the liquid enthalpy departure from the ideal gas enthalpy

The simple model for the enthalpy departure is given by:

$$\Delta H_v = A + B(T - T^{ref})$$

$$\Delta H_L = C + D(T - T^{ref}) \quad (21)$$

where the departures are modeled in terms of energy per unit mass.

The I/O algorithm has four different levels of intermediate iteration printout. These are *None*, *Part*, *Estimate*, and *All*. *None* results in no iteration printout. *Part* results in partial intermediate printout, and is useful to monitor the progress of the algorithm toward solution. *Estimate* should be used to debug a non-converged column. Estimate prints the initial column estimate and more information on actual equation errors to help determine what the convergence difficulty is. *All* prints out the column temperature, liquid and vapor profiles at each iteration and the same comprehensive intermediate printout as *Estimate*.

With *Partial* intermediate printout, the following information is provided at each iteration:

```
ITER    1 E(K) = 1.0717E-01 E(ENTH+SPEC)=1.392E-03 E(SUM) = 3.159E-01
          INNER  0  : E(ENTH+SPEC) = 1.104E-02
          INNER  1  : E(ENTH+SPEC) = 1.854E-04 ALPHA = 1.0000
ITER    2 E(K) = 1.137E-02 E(ENTH+SPEC) = 1.854E-04 E(SUM) = 2.454E-02
          INNER  0  : E(ENTH+SPEC) = 5.925E-04
          INNER  1  : E(ENTH+SPEC) = 7.476E-06  ALPHA = 1.0000
```

The error E(ENTH+SPEC) is the sum of the enthalpy balance and specification errors and is used to determine convergence of the inner loop. The inner loop convergence tolerance for E(ENTH+SPEC) is:

Iteration	E(ENTH+SPEC) Tolerance
1	0.01
2	0.001, (if E(ENTH+SPEC) error from iter 1 was below 0.001, then the tolerance = 2.0E-5)
3	2.0E-5

E(ENTH+SPEC) is the most important number to watch for column convergence.

The second most important number to watch for information about column convergence is alpha, the damping factor. The damping factor alpha is applied to the correction to the stripping factors and sidestream withdrawl factors. An alpha value of 1.0 corresponds to no damping and indicates that convergence is progressing well. Low alpha values indicate that the full correction to the stripping factors resulted in an increase in the inner loop enthalpy and specification equations. A line search is performed using a progressively smaller step size until the inner loop equation errors are reduced. This may be due to a poor approximation to the Jacobian matrix, a very poor starting estimate, or infeasible design specifications.

The E(K) error is the average error between the K-values predicted using the simple thermodynamic model and the rigorously computed K-values using the compostions and termperatures resulting from the inner loop calculations. A large E(K) indicates highly compostion sensititve K-values.

The error sum E(SUM) is the sum of the enthalpy, specification and the bubble point errors. This value is not used in the convergence check. E(SUM) is a good indicator of how convergence is progressing, and is similiar to the ERROR SUM for the Sure Algorithm.

With *Estimate* and *All* iteration printout levels, the following intermediate printout results:

```
ITER 1 E(K) = 1.017E-01 E(ENTH+SPEC)= 1.392E-03 E(SUM   ) = 3.159E-01
        COMPONENT ERROR: AVG = 4.491E-02 MAX(T 1        ) = 1.814E-01
        ENTHALPY  ERROR:  AVG = 0.000E+00 MAX(T 4, LIQ  ) = 0.000E+00
        K-VALUE  ERROR:  AVG = 1.017E-01 MAX(T 1, C 1   ) = 3.31OE-01
        INNER  0 : E(ENTH+SPEC) = 1.104E-02
            SPEC ERROR : AVG = 1.134E-02 MAX(SPEC 1    ) =  2.267E-02
            HBAL ERROR : AVG = 5.368E-03 MAX(TRAY 2    ) = -1.230E-02
            TEMP CHANGE: AVG = 8.500E-01 MAX(TRAY 1    ) = -2.461e+00
        INNER 1: E(ENTH+SPEC) = 1.854E-04    ALPHA - 1.0000
            SPEC ERROR : AVG = 1.886E-04 MAX(SPEC 1    ) =  3.756E-04
            HBAL ERROR : AVG = 9.114E-05 MAX(TRAY 3    ) =  2.182E-04
            TEMP CHANGE: AVG = 1.257E-01 MAX(TRAY 1    ) = -2.431E-01
ITER 2 E(K) = 1.137E-02 E(ENTH+SPEC) = 1.854E-04  E(SUM ) = 2.454E-02
        COMPONENT ERROR: AVG = 5.068E-03 MAX(T  1       ) = 1.026e-02
        ENTHALPY ERROR: AVG = 0.000E+00 MAX(T  4, LIQ    ) = 0.999E+00
        K-VALUE  ERROR: AVG = 1.137E-02 MAX(T  1, C 2    ) = 2.268E-02
          INNER 0 : E(ENTH+SPEC) = 5.9253E-04
            SPEC ERROR : AVG = 6.25E-04 MAX(SPEC  1     ) = -1.247E-03
            HBAL ERROR : AVG = 2.799E-04 MAX(TRAY 2     ) =  5.961E-04
            TEMP CHANGE: AVG = 3.719E-02 MAX(TRAY 1     ) = -8.621E-02
          INNER 1 : E(ENTH+SPEC) = 7.476E-06  ALPHA = 1.0000
            SPEC ERROR : AVG = 8.569E-06 MAX(SPEC 1     ) = -1.587E-05
            HBAL ERROR : AVG = 3.191E-06 MAX(TRAY 2     ) =  9.271E-06
            TEMP CHANGE: AVG = 7.271E-03 MAX(TRAY 1     ) =  1.253E-02
```

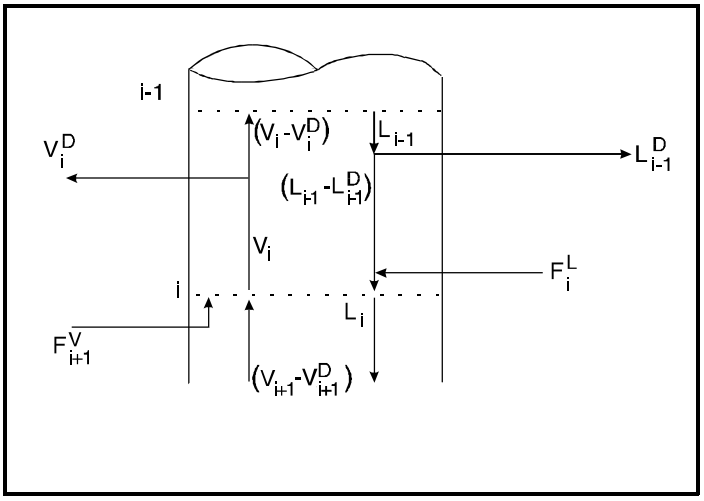
Reference

Russell, R.A., A Flexible and Reliable Method Solves Single-tower and Crude-distillation -column Problems, 1983, *Chem. Eng.*, **90**, Oct. 17, 53-9.

Chemdist Algorithm

The Chemdist algorithm in PRO/II is a Newton based method which is suited to solving non-ideal distillation problems involving a smaller number (10 vs. 100) of chemical species. These conditions are generally encountered in chemical distillations as opposed to crude fractionation where the I/O algorithm would be a better choice. Chemdist is designed to handle both vapor-liquid and vapor-liquid-liquid equilibrium problems as well as chemical reactions.

Figure 2.4.1-3: Schematic of a Simple Stage for Chemdist



Basic Algorithm

Figure 2.4.1-3 shows a schematic of an equilibrium stage for the case of two phase distillation with no chemical reaction. The equations which describe the interior trays of the column are as follows:

Component Mass Balance:

$$M_{i,j} = \exp(X_{i,j})L_i + \exp(Y_{i,j})V_i - \exp(X_{i-1,j})\left(L_{i-1} - L^D_{i-1}\right) \quad (22)$$
$$-exp\,(Y_{i+1,j})\left(V_{i+1} - V^D_{i+1}\right) - f^L_{i,j} - f^V_{i-1,j} \quad i=1, NT, j=1, NC$$

Energy Balance:

$$E_i = L_i\hat{H}^L_i + V_i\hat{H}^V_i - \left(L_{i-1} - L^D_{i-1}\right)\hat{H}^L_{i-1} - \left(V_{i+1} - V^D_{i+1}\right)\hat{H}^V_{i+1} \quad (23)$$
$$-Q_i - F^L_i\,\hat{H}^{FL}_i - F^V_{i+1}\,\hat{H}^{FV}_{i+1}, \quad i=1, NT$$

Vapor-Liquid Equilibrium:

$$Q_{i,j} = Y_{i,j} - X_{i,j} - ln(K_{i,j}) \qquad i = 1,NT \text{ and } j = 1,NC \quad (24)$$

Summation of Mole Fractions:

$$S_i = 1 - \sum_{j=1}^{NL} \exp(X_{i,j}) \qquad i = 1,NT \quad (25)$$

$$S'_i = 1 - \sum_{j=1}^{NC} \exp(Y_{i,j}) \qquad i = 1,NT \quad (26)$$

where:

F_i = total feed flow to tray i
L_i = total liquid flow from tray i
V_i = total vapor flow from tray i
Q_i = heat added to tray i
T_i = temperatures of tray i
$X_{i,j}$ = $\ln(x_{i,j})$ natural log of the liquid mole fractions
$Y_{i,j}$ = $\ln(y_{i,j})$ natural log of the vapor mole fractions
NC = number of components
NT = number of trays

subscripts:

i = tray index
j = component index

superscripts:

F = refers to a feed

D = refers to a draw

L = refers to a liquid property

V = refers to a vapor property

other:

^ refers to properties on a molar basis

lower case letters refer to component flows

upper case letters refer to total flows or transformed variables

The unknowns, alternatively referred to as iteration or primitive variables:

$$(\underline{X}, \underline{Y}, L, V, T)_i \text{, where } i = 1,NT$$

are solved for directly using an augmented Newton-Raphson method. Specification equations involving the iteration variables are added directly to the above equations and solved simultaneously.

The modifications of the Newton-Raphson method are twofold. The first is a line search procedure that will, when possible, decrease the sum of the errors along the Newton correction. If this is not possible, the size of the increase will be limited to a prescribed amount. The second modification limits the changes in the individual iteration variables. Both of these modifications can result in a fractional step in the Newton direction. The fractional step size, is reported in the iteration summary of the column output. Note that an α of 1 indicates that the solution procedure is progressing well and that, as the solution is approached, α should become one. In the case of very non-linear systems which may oscillate, the user can restrict the step size by specifying a damping factor which reduces the changes in the composition variables. A cutoff value is used by the algorithm so that when the value of the sum of the errors drops below the given level, the full Newton correction is used. This serves to speed the final convergence.

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PRO/II Note: For more information on using the damping factor and setting the size of the error increase, see Section 74, *Chemdist*, of the *PRO/II Keyword Input Manual*.

The iteration history also reports the largest errors in the mass balance, the energy balance, and the vapor-liquid equilibrium equations. Given a good initial estimate, these should decrease from iteration to iteration. However, for some systems, the errors will temporarily increase before decreasing on the way to finding a solution. The user can limit the size of the increase in the sum of the errors.

All derivatives for the Jacobian matrix are calculated analytically. User-added thermodynamic options that are used by Chemdist must provide partial derivatives with respect to component mole fractions and temperature. Chemdist uses the chain rule to convert these to the needed form.

Vapor-Liquid-Liquid Algorithm

The equations describing the VLLE system are derived by substituting the bulk liquid flows and transformed bulk liquid mole fractions, $\overline{L}_i$ and $\overline{X}_{i,j}$, for the single liquid phase flows and the transformed liquid mole fractions, L_i and $X_{i,j}$, in the above equations (22-26).

That is, L_i becomes $\overline{L}_i$ and $X_{i,j}$ becomes $\overline{X}_{i,j}$.

where:

$$\overline{X}_{i,j} = \ln\left((l'_{i,j} + l''_{i,j})/(L'_{i,j} + L''_{i,j})\right) \quad (27)$$

$$\overline{L}_i = L'_i + L''_i \quad (28)$$

and:

L'_i , L''_i = total liquid flows of the first and second liquid phases, respectively.

$l'_{i,j}$, $l''_{i,j}$ = component liquid flows in the first and second liquid phases, respectively.

The new equations which are identical in form to those listed in the basic algorithm section above, equations (22-26), will not be repeated here. The K-values which are used in the VLE equations are calculated by performing a LLE flash. That is, the K-value is evaluated at the composition of one of the liquid phases produced by the LLE flash. Chemdist uses the K-value derivatives with respect to the two liquid phases, the chain rule, and the definition of a total derivative to calculate the derivatives of the VLE equation with respect to the bulk liquid flow and composition. That is, the bulk liquid flows are subject to the all of the constraints imposed by the LLE equations.

The equations are solved in a two-step approach. After initialization and calculation of the Jacobian matrix, the Newton-Raphson algorithm calculates new values for the iteration variables ($\underline{X}$, $\underline{Y}$, L , V , T)$_i$. The resulting tray temperatures and composition of the bulk liquid phases are used in performing liquid-liquid equilibrium flash calculations. If a single liquid phase exists, the calculations proceed as in the basic algorithm. If a second liquid phase is detected, the liquid compositions of the two liquid phases are used to calculate the K-values and the derivatives with respect to each liquid phase. Using the chain rule and the definition of a total derivative, these composition derivatives are used to calculate the derivative of the VLE equations with respect to the bulk liquid phase. A new Jacobian matrix is calculated and the Newton-Raphson algorithm calculates new values for the iteration variables. The cycle repeats until convergence is achieved.

This approach is not as direct as using the individual component compositions for each liquid phase. However, it results in more stable performance of the Newton-Raphson algorithm because a second liquid phase is not continually appearing and disappearing. Liquid draws are dealt with in terms of bulk liquid properties (i.e., other than for a condenser, it is not possible to directly specify the selective withdrawal of any one liquid phase).

References:

1. Bondy, R.W., 1991, Physical Continuation Approaches to Solving Reactive Distillation Problems, paper presented at 1991 AIChE Annual meeting.
2. Bondy, R.W., 1990, A New Distillation Algorithm for Non-Ideal System, paper presented at AIChE 1990 Annual Meeting.
3. Shah, V.B., and Bondy, R.W., 1991, A New Approach to Solving Electrolyte Distillation Problems, paper presented at 1991 AIChE Annual meeting.

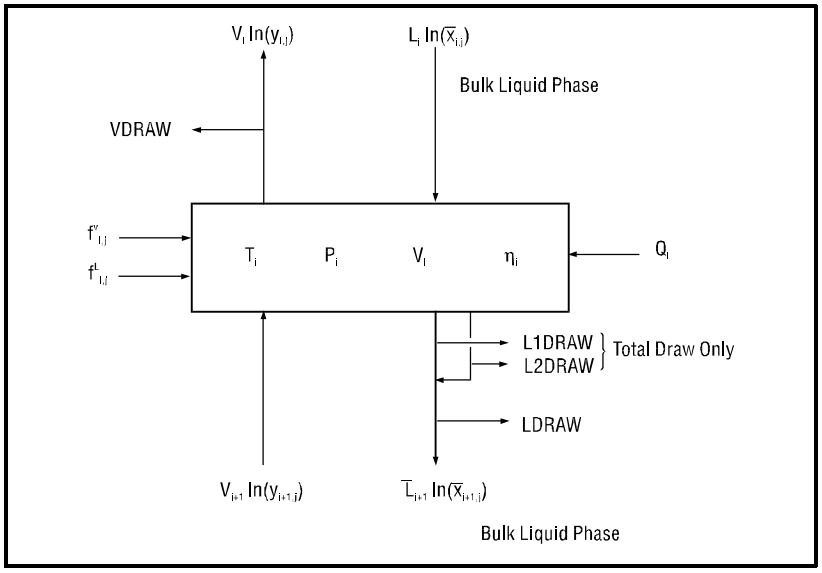
Reactive Distillation Algorithm

The Chemdist and LLEX algorithms in PRO/II support both liquid and vapor phase chemical reactions. Since reactiive distillation is an extension of the basic chemicals distillation algorithm, the reader should be familar with this material before proceeding. In general, the extensions of the Chemdist and LLEX algorithms for reactive distillation are suited to the same size systems, i.e., distillation systems which have a smaller number (10 vs. 100) of chemical species. Larger systems can be simulated, but a large number of calculations can be expected.

Basic Algorithm

Figure 2.4.1-4 shows a schematic of an equilibrium stage for the case of two-phase distillation with chemical reaction. The equations which describe the interior trays of the column on which reactions occur are essentially the basic equations which have terms added for generation and consumption of chemical species. The equilibrium equations will be affected only indirectly through the formation or disappearance of chemical species. Similarly, the energy balance equation is affected through the enthalpies of the species enthalpies. If two chemicals react to form a third and produce heat in doing so, then the enthalpy of the reaction product must be low enough to account for the disappearance of the moles of the reacting species and the heat of reaction.

Figure 2.4.1-4: Reactive Distillation Equilibrium Stage



The mass balance equations are the only equations which must have consumption and production terms added. The new equation is:

(29)

$$M_{i,j} = \exp(X_{i,j})L_j + \exp(Y_{i,j})V_j - \exp(X_{i,j-1})L_{j-1} = \exp(Y_{i,j}+1)V_{j+1} - \sum_{k=1}^{NF} F_k Z_{i,k}$$

$$- \sum_{k=1}^{N_{RxKj}} V_{i,k} r_k - \sum_{k=1}^{N_{RxEq}} V_{i,k}\,\varepsilon - \sum_{k=1}^{N_{RxCnv}} \frac{V_{i,k}}{V_{Ref,k}}\,\varepsilon\left(\exp(X_{Ref,j-1})L_{j-1} + \exp(Y_{Ref,j+1})V_{j+1}\right)$$

The kinetic rates of reaction are given by:

(30)

$$r_k = k_0 \exp^{\left(\frac{A}{RT}\right)} V \prod [A]^a [B]^b K$$

where:

V = the reaction volume

A, B = denote chemical species A and B

a,b = the stoichiometric coefficients of chemical species A and B in the stoichiometric equation, respectively

$\exp(-A/RT)$ = the Arrhenius rate expression for temperature dependence

Π = denotes the product of the concentrations of the chemicals raised to their stoichiometric coefficients.

The only place the reaction volume is used in the distillation calculations is in the kinetic rate expression (equation (30)). It is extremely important that the tray reaction volumes are consistent with the volume basis used in determining the kinetic rate expression. If the reaction is a homogeneous liquid phase reaction, and the rate expression is based on liquid phase reactions done in a CSTR, then the liquid volume should be used. This volume corresponds to the liquid volume on the tray and in the downcomer. Do not use the entire mechanical volume between trays unless the rate expression was determined from pilot plant data and the entire volume was used to characterize the rate equation. Similarly, if the reaction is catalyzed by a metal on a ceramic support and the rate equation was based on the entire cylindrical volume of the packed bed holding the catalyst, then this should be used.

Since the enthalpy basis in PRO/II is on a pure chemical basis, it is unsuitable for keeping track of enthalpy changes due to reactions. Therefore, reactive distillation converts chemical enthalpies to an elemental basis before simulating the tower. After the simulation is complete, the product stream enthalpies are recalculated using the standard PRO/II basis. While this is mostly hidden from the user, it does impact the reporting overall column enthalpy balance and is the reason for reporting multiple enthalpy balances. This does *not* impact the accuracy of the solution.

Chemdist and LLEX support any type of reaction which can be entered through the Reaction Data section or described using an in-line procedure. Various reaction parameters may be varied from the flowsheet using calculators and DEFINE statements. Any set of mixed reactions may be assigned to trays in the distillation column.

Chemdist and LLEX support single tray distillation columns. By using this feature, Chemdist may be used as a two-phase reactor model which produces vapor and liquid streams in equilibrium. In addition, the bottoms product rate may be set to zero so that a boiling pot reactor can be modeled. As part of this functionality, a single non-volatile component may be specified. The non-volatile component is typically a catalyst which may used in the kinetic reaction rate expressions.

Kinetic Reaction Homotopy (Volume Based)

The solution of the Mass, Equilibrium, Summation, and Enthalpy balance equations can be a difficult task for non-ideal chemical systems. The addition of reaction terms further complicates the challenge. Chemdist and LLEX both have a homotopy procedure to simplify obtaining a solution to reactive distillation columns. The basic procedure is straightforward:

- Start with a set of equations to which you know the answer.
- Then modifiy the equations a little and solve them.
- Modify them again and re-solve using the last solution.

Eventually, the equations will be deformed into the equations to which you want the answer.

This procedure has a formalized mathematical basis with the theoretical underpinings beginning as early as 1869 (Ficken, 1951). Mathematically, a homotopy is a deformation or bending of one set of equations that are difficult to solve, f{x} = 0, into a set whose solution is known or easily found, g{x}=0. A new set of equations, referred to as the homotopy equations, is constructed from f{x} and g{x}. The homotopy equations are what enable us to move smoothly from the easy problem to the difficult problem. The most general conditions for the homotopy equation are:

$$H[x,t] = \text{some function of } f[x] \text{ and } g[x] = 0 \qquad (31)$$

such that:

$$H[x^0,0] = g[x^0] = 0$$
$$H[x*,1] = f[x*] = 0$$

The simplest transformation is a linear homotopy. In this case, the homotopy equation becomes:

$$H[x,t] = tf[x] + (1-t)\, g[x] = 0 \qquad (32)$$

In equation (32), t is varied from zero to 1. The first challenge is choosing the proper homotopy, the second is determining the sequence of t that allows you to move from the simple equations to the difficult equations.

The methods for tracking the homotopy path from 0 to 1 are classified as either ‘‘simplicial’’, discrete methods, or ‘‘continuation’’, differential methods based on the integration of an initial value method. Currently, the reactive distillation algorithm in PRO/II uses a ‘‘classical’’ homotopy with a set of predefined steps. In most cases involving reaction, this approach is sufficient.

The reactive distillation algorithm uses a physical homotopy with the reaction volume being linked directly to the homotopy parameter. That is, initially, the reaction volume is zero and the ‘‘simple’’ set of equations corresponds to the basic distillation problem. At the final point, the reactive volume is equal to the specified volume and the equations are the full set describing reactive distillation. This homotopy is only used for those systems using a reaction volume. These are the most difficult systems to solve.

The actual function used to increase the reaction volume is a combination of functions. Initially, there may not be any products present in the tower and the reaction may proceed very quickly. Therefore, the volume is initially increased on a log fraction basis which very gradually introduces the reaction. After the products begin to accumulate on the trays, the reaction volume is increased linearly. The transition between the two modes is at 25%.

Summarizing, if the reaction homotopy is used, the initial problem is solved with no chemical reaction on the trays. After the solution is reached, the reaction volume is increased by a small amount and the problem is resolved using the no reaction solution as a starting point. After the solution is reached, the reaction volume is again increased and the problem is resolved. This continues until the reaction volume has been fully introduced. The number of increments and the initial volume may be specified by the user.

If the steps are small or the problem is not particularly difficult, the problems at each volume are solved in a small number of iterations. Even with this, the distillation equations are being solved at each volume step and it may take quite a few iterations to solve. Other authors report increases in solution times from 30% to 300% depending on the difficulty of the problem. In fairness, if the problem takes 3 times as long using the homotopy, the engineer devoted a great deal of time generating the initial estimates in order to get any solution. In many cases, there is no choice.

References

1. Bondy, R.W., Physical Continuation Approaches to Solving Reactive Distillation Problems, paper presented at 1991 AIChE Annual meeting.

2. Ficken, F.A., 1951, The Continuation Method for Functional Equations, Communications on Pure and Applied Mathematics, 4.

Initial Estimates

As previously mentioned, initial column profiles are needed for solution of the column heat, mass, equilibrium, and performance specification balances. These may either be provided by the user, or generated internally by PRO/II using an initial estimate generator.

User-provided Estimates

Ideally, the only estimates the user has to provide is either the overhead rate or the bottoms rate with the product information. On the other extreme, the user can provide the complete estimates for the temperature, flowrates, and composition profiles. PRO/II's initial estimate generation (IEG) algorithms generate these numbers relatively well and the user need not provide any initial estimates except for difficult simulations.

PRO/II could interpolate the temperature, liquid and vapor rates, and phase compositions estimates, if the end point values for these variables are available. These end point values could either be provided by the user or estimated by PRO/II. When these values are provided by the user, we require that the user provide at least two endpoint values (first and last theoretical stage). The first theoretical stage is the condenser or the top tray for the ''no condenser'' case. The last theoretical stage is the reboiler or the bottom tray for the ''no reboiler'' case.

Temperatures

Tray temperatures are relatively easy to estimate. The reboiler and condenser temperatures represent the bubble points and/or dew points for the products. These may be estimated by the user or calculated using the shortcut fractionator model.

The top and bottom tray temperatures may be estimated by addition or subtraction of a reasonable temperature difference from the condenser and reboiler temperatures.

For complex fractionators, the product draw temperatures are usually known or can be estimated from the product ASTM distillations.

Liquid and Vapor Profiles

For most columns, the vapor and/or liquid profiles are more difficult to estimate. Moreover, they are generally more influential than temperatures in aiding or hindering the solution.

Estimates for the overhead or the bottoms products are provided with the product information; in addition, rates for the side draw products are also provided by the user.

For columns with condensers, it is important to provide an estimate of the reflux, either as the liquid from tray one or the vapor leaving tray two (the top product plus reflux). For simple columns with liquid or moderately vaporized feeds, constant molar overflow may be assumed and the vapor from the reboiler tray 6 assumed to be the same as the tray 2 vapor. The reboiler vapor may also be provided by giving an estimate of the liquid leaving the tray above the reboiler.

For columns in which the feed has high vapor rate, there will be a sharp break in the vapor profile at the feed tray. For such columns at least four vapor rates should be provided: top tray, feed tray, tray below feed, and bottom tray.

For columns in which the reflux is to be used as a performance specification, the reflux should be set at the specification value in the estimate, enhancing convergence.

The effect of side draws must be considered for complex fractionators. It is usually safe practice for such columns to add the side product rates and multiply by two to estimate a top reflux rate.

For columns having steam feeds, the steam flow must be included in the vapor estimates. An estimate of the decanted water should also be included with the product information.

Note: In general, convergence is enhanced when the reflux quantity is estimated generously.

Liquid and Vapor Mole Fractions

PRO/II generates reasonable profiles for liquid and vapor mole fractions, using one of the initial estimate models selected by the user. The user could provide the mole fraction profile to aid the convergence.

Estimate Generator

The temperature, rate, and composition profiles not provided by the user are generated by PRO/II using one of the built-in estimate generator models. When using the estimate generator, product rates are still provided with the product information.

Various models used for the estimate generation are shown below in Table 2.4.1-2 with the column algorithm.

Table 2.4.1-2: Default and Available IEG Models

Algorithm/ IEG Method	I/O	Chemdist	SURE	LLEX	ELDIST
Simple	Default	Default	Default	Default	Yes*
Conventional	Yes	Yes	Yes		
Refining	Yes	Yes	Yes		
Electrolyte					Default*

* For electrolytic systems, simple IEG is same as electrolyte IEG.

The estimate generator will work for most columns, regardless of complexity or configuration. Of course, for simulations in which a column model is being used to simulate a combination of unit operations (columns, flash drums, etc.), the estimate generator should not be used since it sets up profiles corresponding to a conventional distillation situation. Furthermore, use of the estimate generator is not meant to provide the most optimum starting point (although this may often be the case) but rather to provide a starting point with a high probability of reaching solution.

The *Simple* estimate generator computes tray flows from constant molar overflow and the temperatures and mole fractions from L/F flashes.

The *Conventional* estimate generator uses the Fenske method to determine product mole fractions as follows:

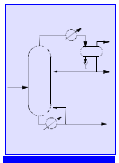
- Perform shortcut Fenske calculations to determine the product splits and compositions. The flows from the product information are used to initiate the shortcut calculations and, when possible, the performance specifications desired for the rigorous solution will be used for specifications. Note that only specifications pertaining to the product rates or compositions have any meaning for the shortcut model, i.e., rigorous specifications such as tray temperatures and tray flows (including reflux) have no meaning. When rigorous specifications cannot be used, the initial estimate generator will use alternate specifications selected in this order: the rate from the product information, and a fractionation index (Fenske trays) equal to approximately 1/2 of the column theoretical trays.
- Based on the shortcut results the product temperatures are calculated. Any user-provided temperatures are used directly.
- The column liquid loading is calculated by using the reflux estimate provided by the user. Note that an L/D ratio of 3.0 is assumed if no reflux quantity is provided.
- A column heat balance is performed. If side coolers are present and duties have been provided, the flow profiles are appropriately adjusted.

The *Refining* estimate generator uses the Fenske method just like the conventional estimate generator. The four steps described above for the conventional method are repeated here. In addition, the bottom tray temperature is adjusted for the effect of stripping stream, if present. Adjustment is also made for inter-linked columns if present.

In light of the above procedure it is good practice to:

Recommendations

- Provide reasonable estimates with the product information.
- Provide a reasonable reflux estimate.
- Provide temperature guesses for subcooled products (the estimate generator would use the saturated values).
- Provide the side cooler/heater estimates, if possible.



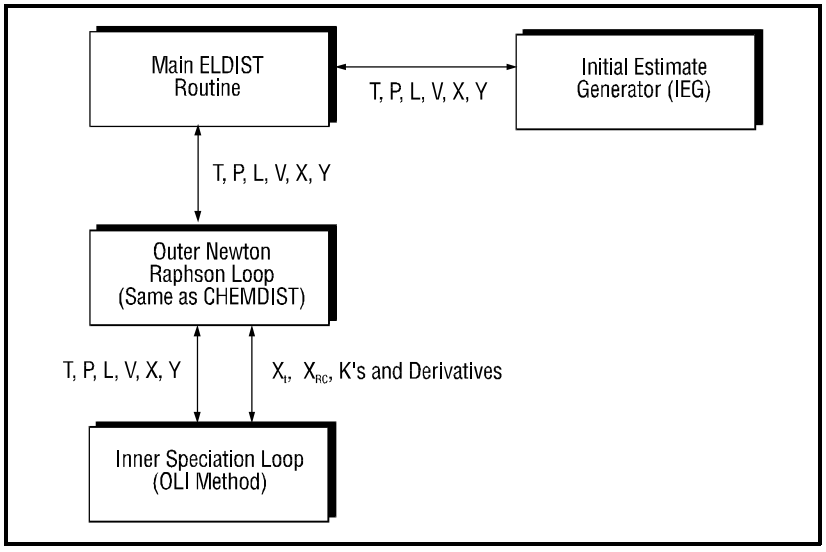
2.4.2 ELDIST Algorithm

The ELDIST algorithm in PRO/II is a combination of a Newton-based method which is used in Chemdist for solving MESH equations and the solution of liquid phase speciation equations described in Section 1.2.9, *Electrolyte Mathematical Model*.

Basic Algorithm

Column mesh equations are solved by a Newton-Raphson algorithm in the outer loop while liquid phase speciation along with K-value computations are handled by the inner loop, as shown in Figure 2.4.2-1.

Figure 2.4.2-1: ELDIST Algorithm Schematic


Main ELDIST Routine
T, P, L, V, X, Y
Initial Estimate Generator (IEG)
T, P, L, V, X, Y
Outer Newton Raphson Loop (Same as CHEMDIST)
T, P, L, V, X, Y
X_i, X_{RC}, K's and Derivatives
Inner Speciation Loop (OLI Method)

Inner Speciation Loop

Input to the inner loop model are temperature, pressure, and component mole fractions for liquid and vapor phase. Temperature, pressure, and liquid phase mole fractions are needed for speciation calculations and for computation of liquid phase fugacities. Vapor phase mole fractions, along with the above information, are needed for K-value and K-value derivatives computations.

To better describe the liquid phase speciation concept, consider the aqueous system of components H_2O, CO_2, and NaCl. If NaCl precipitation is not allowed then there are eight unknowns for a given system. These are:

$Moles_{H2O}$, M_{HION}, M_{OHION}, $M_{HCO3ION}$, M_{NAION}, M_{CLION}, and M_{CO2AQ}

(M is molality (moles per kg solvent) of a component or an ion)

There are three independent equilibrium equations:

$$K_{H2OAQ} = \frac{\gamma_{HION} \bullet m_{HION} \bullet \gamma_{OHION} \bullet m_{OHION}}{a_{H2OAQ}} \quad (1)$$

$$K_{H2OAQ} = \frac{\gamma_{HION} \bullet m_{HION} \bullet \gamma_{HCO3ION} \bullet m_{HCO3ION}}{\gamma_{CO2AQ} \bullet m_{CO2AQ} \bullet a_{H2OAQ}} \quad (2)$$

$$K_{HCO3ION} = \frac{\gamma_{HION} \bullet m_{HION} \bullet \gamma_{CO3ION} \bullet m_{CO3ION}}{\gamma_{HCO3ION}\, m_{HCO3ION}} \quad (3)$$

where:

γ = activity coefficients

K = equilibrium constants

Activity coefficients and equilibrium constants are functions of temperature, pressure and molarities of components or ions.

In addition, there are four independent atom balance equations and one electroneutrality equation.

Sodium Balance:

$$NaCl(In) - m_{NAION} \bullet Moles_{H2O} \bullet MW_{H2O} / 1000. = 0. \quad (4)$$

Chlorine Balance:

$$NaCl(In) - m_{CLION} \bullet Moles_{H2O} \bullet MW_{H2O} / 1000. = 0. \quad (5)$$

Carbon Balance:

$$CO_2(In) - \left(m_{CO3ION} + m_{HCO3ION} + m_{CO2AQ}\right) Moles_{H2O} \bullet MW_{H2O} / 1000. = 0. \quad (6)$$

H^+ Balance:

$$H_2O(In) - Moles_{H2O} - \left(Moles_{H2O} \bullet MW_{H2O} / 1000.\right) \bullet \left(m_{CO3ION} + m_{OHION} + m_{HCO3ION}\right) = 0. \quad (7)$$

Electroneutrality Equation:

$$(m_{HION} + m_{NAION}) - (M_{HCO3ION} + 2m_{CO3ION} + m_{OHION} + m_{OLION}) = 0. \quad (8)$$

The inside loop solves these eight equations for eight unknowns using Newton's method. Once these unknowns are computed, and true (aqueous) mole fractions of aqueous components are determined, all ions are combined to translate them in terms of aqueous mole fractions of the original components. These components are referred to as *Reconstituted Components*. Overall mole fractions for these components would be the aqueous mole fractions (true mole fraction) plus reconstitution of ions. Hence, for a given set of input liquid mole fractions ($\underline{x}$), the inside loop returns two sets of liquid mole fractions, namely the true mole fractions ($\underline{x}$), and the reconstituted mole fractions ($\underline{x}_{RC}$).

Once the speciation equations are solved, vapor-liquid equilibrium constants (K-values) and its derivatives are computed as a function of T, P, X_t, and y.

Outer Newton-Raphson Loop

Outer loop model is solved by the Newton-Raphson algorithm. There are 2NC+3 equations and 2NC+3 unknowns on each theoretical tray.

Independent variables on each tray are:

a.	Natural log of liquid mole fractions,	ln (x)	NC
b.	Natural log of vapor mole fractions,	ln (y)	NC
c.	Tray liquid rate L		1
d.	Tray vapor rate V		1
e.	Tray temperature T		1
			2NC+3

The equations to be solved on each tray are:

Component Balance: (NC)

$$mb(n,j) = x(n-1,j)L(n-1) + y(n+1,j)V(n+1) + f(n,j) - y(n,j)\,(V(n) + Sv(n)) \qquad (9)$$

$$- x(n,j)(L(n) + SL(n)) = 0.$$

Vapor-Liquid Equilibrium: (NC)

$$vle(n,j) = \ln(y(n,j)) - \ln(k,(n,j)x(n,j)) = 0. \qquad (10)$$

Energy Balance: (1)

$$Eb(n) = F(n)Hf(n) + V(n-1)H(n-1) + L(n+1)h(n+1) \qquad (11)$$

$$- (V(n) + SV(n))H(n) - (L(n)+SL(n))h(n) + Q(n) = 0.$$

Summation x: (1)

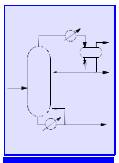
$$SX(n) = \left(\sum_j x(n,j) \right) - 1 = 0. \qquad (12)$$

Summation y: (1)

$$SY(n) = \left(\sum_j y(n,j) \right) - 1 = 0. \qquad (13)$$

References:

1. Shah, V.B., Bondy, R.W., A New Approach to Solving Electrolyte Distillation Problems, paper presented at 1991 AIChE annual meeting.
2. OLI Systems Inc., 1991, PROCHEM User's Manuals, Version 9, Morris Plains, NJ.



2.4.3 Column Hydraulics

General Information

PRO/II contains calculation methods for rating and sizing trayed distillation columns, and for modeling columns packed with random or structured packings. Trayed columns are preferable to packed columns for applications where liquid rates are high, while packed columns are generally preferable to trayed columns for vacuum distillations, and for corrosive applications. All tray rating and packed column calculations require viscosity data. A thermodynamic method for generating viscosity data from Table 2.4.3-1 should therefore be selected by the user for these applications.

Table 2.4.3-1: Thermodynamic Generators for Viscosity

Method	Phase
PURE	VL
PETRO	VL
TRAPP	VL
API	L
SIMSCI	L
KVIS	L

Tray Rating and Sizing

Columns containing valve, sieve, or bubble cap trays may be modeled by PRO/II using a number of proven methods. Methods developed by Glitsch are used to compute the capacity or flood point, and the pressure drop for valve trays. For sieve or bubble cap trays, the capacity is computed by using 95 and 85% of the valve capacities respectively. The tray pressure drop is calculated by the Fair method for sieve trays, and by the method of Bolles for bubble cap trays.

Capacity

The capacity of a trayed column is defined in terms of a vapor flood capacity factor, at zero liquid load, CAF_0. Nomographs are used to obtain the capacity factors based on tray spacing and vapor density.

Foaming on trays is taken into account by using a so-called ‘‘system factor’’. Table 2.4.3-2 shows the system factors to be used to correct the vapor capacity factors.

Table 2.4.3-2:
System Factors for Foaming Applications

System	Factor
Absorbers (over 0 °F)	.85
Absorbers (below 0 °F)	.80
Amine Contactor	.80
Vacuum Towers	.85
Amine Stills (Amine Regenerator)	.85
H_2S Stripper	.85
Furfural Fractionator	.85
Top Section of Absorbing Type Demethanizer/Deethanizer	.85
Glycol Contactors	.50
Glycol Stills and Glycol Contactors in Glycol Synthesis Gas	.65
CO_2 Absorber	.80
CO_2 Regenerator	.85
Caustic Wash	.65
Caustic Regenerator, Foul Water, Sour Water Stripper	.60
Alcohol Synthesis Absorber	.35
Hot Carbonate Contactor	.85
Hot Carbonate Regenerator	.90
Oil Reclaimer	.70

For sizing an existing trayed column, or for calculating the percent of flood for a given column diameter, the column vapor load is used. The vapor load may be determined by using:

$$Vload = ACFS\,(\rho_G / (\rho_L - \rho_G))^{0.5} \qquad (1)$$

where:

Vload = vapor load capacity

ACFS = actual vapor volumetric flow rate

ρ_G = vapor density

ρ_L = liquid density

Pressure Drop

For valve, sieve, or bubble cap trays the total tray pressure drop is a sum of the dry tray pressure drop, and the pressure drop due to the liquid holdup on the trays:

$$\Delta P = \Delta P_{dry} + \Delta P_l \qquad (2)$$

where:

ΔP = total pressure drop, inches liquid

ΔP_{dry} = dry tray pressure drop, inches liquid

ΔP_l = pressure drop through the liquid on the trays, inches liquid

The dry tray pressure drop is obtained from nomographs relating the pressure drop to the weight of the valves at low vapor flow rates, and to the square of the vapor velocity at high vapor flow rates.

For sieve trays, the method of Fair is used to calculate the dry tray pressure drop, which is given by:

$$\Delta P_{dry} = 0.186 / C_v^2 \, (\rho_G / \rho_L) v_G^2 \qquad (3)$$

where:

C_v = discharge coefficient

v_G = superficial vapor velocity

For bubble cap trays, the dry tray pressure drop is calculated by the method of Bolles:

$$\Delta P_{dry} = 1.20(\rho_G / (\rho_L - \rho_G))^{0.2} \, h_{sh} \, v_G^{0.4} + K_2 \, \rho_G / \rho_L \, v_G^2 \qquad (4)$$

where:

h_{sh} = bubble cap slot height

The dry cap coefficient, K_2, in equation (4) is a function of the ratio of the annular to riser areas.

For valve trays, the pressure drop through the liquid is given by:

$$\Delta P_l = 0.4 \left((L / l_w)^{2/3} + h_w \right) \qquad (5)$$

where:

L = total liquid flow rate, gpm

l_w = weir length, inches

h_w = weir height, inches

The pressure drop through the liquid on the sieve or bubble cap tray is given by:

$$\Delta P_l = \beta \, h_{ds} \qquad (6)$$

For sieve trays,

$$h_{ds} = h_w + h_{ow} + h_{hg}/2 \qquad (7a)$$

For bubble cap trays,

$$h_{ds} = h_s + h_{ow} + h_{hg}/2 \qquad (7b)$$

where:

h_{ds} = calculated height of clear liquid over trays (dynamic seal)

h_w = weir height

h_s = static slot seal (weir height minus height of top slot above plate floor)

h_{ow} = height of crest over weir

h_{hg} = hydraulic gradient across plate

The dimensionless aeration factor, β, in equation (6) is a function of the superficial gas velocity.

Random Packed Columns

Columns containing conventional randomly oriented or dumped packings such as Raschig rings, Berl saddles, and Pall rings may be modeled by PRO/II. Table 2.4.3-3 shows the random packing types supported by PRO/II.

Table 2.4.3-3
Random Packing Types, Sizes, and Built-in Packing Factors (ft^2/ft^3)

TYPE=	Random Packing Type	(mm) (in) (size)	6.3 0.25	9.5 0.375	12.7 0.5	15.9 0.625 #15	19 0.75	25.4 1.0 #25	31.7 1.25	38.1 1.5 #40	50.8 2.0 #50	76.2 3.0 #70	88.9 3.5
1	IMTP® (Metal)					51		41		24	18	12	
2	Hy-Pak™ (Metal)							45		29	26		16
3	Super Intalox® Saddles (Ceram)							60			30		
4	Super Intalox Saddles (Ceram)							40			28		18
5	Pall Rings (Plastic)					95		55		40	26		17
6	Pall Rings (Metal)					81		56		40	27		18
7	Intalox Saddles (Ceramic)		725	1000	580		145	92		52	40	22	
8	Raschig Rings (Ceramic)		1600	1000	580	380	255	179	125	93	65	37	
9	Raschig Rings (1/32" Metal)		700	390	300	170	155	115					
10	Raschig Rings (1/16" Metal)				410	300	220	144	110	83	57	32	
11	Berl Saddles (Ceramic)		900		240		170	110		65	45		

IMTP and Intalox are registered marks of Norton Company. Hy-Pak is a trademark of Norton Company.

Capacity

The capacity of a randomly packed column is determined by its flood point. The flood point is defined as the point at which the slope of the pressure drop curve goes to infinity, or the column efficiency goes to zero. For random packings, the flood point as given by the superficial vapor velocity at flood, v_{Gf}, is determined by Eckart's correlation:

$$v_{Gf}^2 F_P \varphi \mu_L^{0.2} \rho_G / \rho_L \, g_c = function\left(L' / G' \, (\rho_G / \rho_L)^{0.5}\right) \qquad (8)$$

where:

v_{Gf} = superficial vapor velocity at flood
F_p = packing factor
φ = ρ_w/ρ_L
ρ_w = density of water
ρ_G = density of vapor
ρ_L = density of liquid
g_c = gravitational constant
μ_L = liquid viscosity
L' = liquid mass flux
G' = vapor mass flux

Alternately, the flood point may be supplied by the user.

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PRO/II Note: For more information on supplying a user-input approach to flood using the FLOOD keyword, see Section 77, *Column Hydraulics*, of the *PRO/II Keyword Input Manual*.

Pressure Drop

The column pressure drop may be calculated by one of two methods. The Norton method uses a generalized pressure drop correlation:

$$\Delta P = function_1\left(F_p \nu_L^{0.1} \nu_G^2 \left(\frac{\rho_G}{\rho_L - \rho_G}\right), \frac{L}{G}\left(\frac{\rho_G}{\rho_L}\right)^{0.5}\right) \qquad (9)$$

where:

ν_L = μ_L/ρ_L = liquid kinematic viscosity

The Tsai method uses the following correlation for computing pressure drop:

$$\Delta P = function_2\left(\frac{C_s^2 F_p \nu_L}{g_c}, \frac{L}{G}\left(\frac{\rho_G}{\rho_L}\right)^{0.5}\right) \quad (10)$$

where:

C_s = operating capacity factor = $v_G\left(\frac{\rho_G}{\rho_L - \rho_G}\right)^{0.5}$

However, there are no published packing factors for the Tsai method. Therefore the Norton packing factors are utilized by PRO/II when equation (10) is used.

Efficiency

The column efficiency may be measured by the Height Equivalent to a Theoretical Plate (HETP). The HETPs for most chemical systems are generally close in value for a fixed packing size, regardless of the application. By default, therefore, the HETP values are determined by a ''Rules-of-thumb'' method suggested by Frank.

If Norton IMTP packing is used, an alternate method may be used to compute the HETP values. In this method, more rigorous calculations are made based on the size of the packing and the total vapor and total liquid leaving a packed stage. The height of a vapor phase transfer unit is given by:

$$H_G = \left\{\varphi\,(D_t'/0.3048)^a\,(z_p/3.048)^{1/3}\,(Sc_G)^{0.5}\right\} / \left\{737.34 G_L f_\mu f_\rho f_\sigma\right\}^b \quad (11)$$

where:

H_G = height of vapor phase transfer unit, m

φ = packing parameter

D_t' = lesser of column diameter or 0.6096 m (2 ft)

z_p = height of packed bed, m

Sc_G = gas phase Schmidt number = $\mu_G / \rho_G D_G$

D_G = gas phase diffusion coefficient, m^2/s

G_L = liquid mass velocity based on column cross section, kg/m.s

f_μ = $(\mu_L/\mu_w)^{0.16}$

f_ρ = $(\rho_L/\rho_w)^{-1.25}$

f_σ = $(\sigma_L/\sigma_w)^{-0.8}$

a = 1.24 for ring packings, 1.11 for saddle packings

b = 0.6 for ring packings, 0.5 for saddle packings

The height of a liquid phase transfer unit is given by:

$$H_L = \phi\, C_{fl}\, (z_p / 3.048)^{0.15}\, (Sc_L)^{0.5} \qquad (12)$$

where:

ϕ = packing parameter
C_{fl} = function of F_r
F_r = v_G/v_{Gf} at constant L/V
v_G = superficial vapor velocity, m/s
v_{Gf} = superficial vapor velocity at flood, m/s
Sc_L = liquid phase Schmidt number = $\mu_L/(\rho_L D_L)$
D_L = liquid diffusion coefficient, m^2/s

The HETP is then computed from:

$$HETP = \left(H_G + \lambda H_L\right) \ln(\lambda / (\lambda - 1)) \qquad (13)$$

where:

λ = ratio of slope of equilibrium line to operating line = mV/L

Packing factors for the various random packing types are given in Table 2.4.3-3.

Structured Packed Columns

Columns containing various structured packings manufactured by Sulzer Brothers of Switzerland can be simulated using PRO/II. Column pressure drop, capacity, and efficiency for the 12 different types of Sulzer packings given in Table 2.4.3-4 are computed using correlations supplied by Sulzer.

Table 2.4.3-4:
Types of Sulzer Packings Available in PRO/II

Type	Description	Applications
M125X M125Y	125 m^2/m^3, sheet metal, very high capacity. Suitable for extremely high liquid loads where separation efficiency requirements are low. Configuration angle of X types 30 degree to vertical, Y types 45. Use X types for higher capacity, Y types for higher separation efficiency.	Basic chemicals Ethylbenzene/ styrene Fatty acids, e.g., tall oil Cyclohexanone/ -ol, Caprolactam Vacuum columns in refineries
M170Y	170 m^2/m^3, sheet metal, high capacity, moderate separation efficiency.	
M250X M250Y	250 m^2/m^3, sheet metal, moderate capacity, high separation efficiency.	C_3 splitter, C_4 splitter Absorption/ desorption columns
M350X M350Y	350 m^2/m^3, sheet metal, moderate capacity, high separation efficiency.	
M500X M500Y	500 m^2/m^3, sheet metal, limited capacity, very high separation efficiency. Suitable where column weight is of overriding importance.	
BX CY	Metal wire gauze, high capacity, high separation efficiency even at small liquid loads. CY offers maximum separation efficiency, lower capacity than BX.	Fine chemicals Isomers Perfumes Flavors Pilot columns Increased performance of existing columns
KERA	Thin-walled ceramic KERAPAK packing for corrosive and/or high temperature applications.	Halogenated organic compounds (only limited suitability in the presence of aqueous mineral acid, lay, and aqueous solutions)

Sulzer structured packings available in PRO/II include 9 types of corrugated sheet metal known as MELLAPAK, 2 types of metal gauze known as BX and CY, and a ceramic KERAPAK packing.

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PRO/II Note: For more information on using Sulzer structured packings, see Section 77, *Column Hydraulics*, of the *PRO/II Keyword Input Manual*.

Capacity

The capacity of a packed column is generally limited by the onset of flooding, or maximum column vapor load. The flooding point, however, is difficult to measure. For structured packing, the limit of capacity is generally used to indicate the flood point. The limit of capacity (100% capacity) is defined as the vapor load that corresponds to a column pressure drop of 20 mbar/m.

Furthermore, the column capacity is expressed in terms of the capacity factor. The capacity factor or load factor, c_G, of the vapor phase is defined as:

$$c_G = V_G\left(\rho_G / (\rho_L - \rho_G)\right)^{1/2} \quad (14)$$

where:

V_G = superficial vapor velocity, m/s

ρ_G = vapor density, kg/m^3

ρ_L = liquid density, kg/m^3

Capacity correlations are obtained by plotting the experimental capacity data on a so-called Souder diagram. On this diagram, the capacity factor is plotted versus the flow parameter, φ, which is defined as:

$$\varphi = L / G(\rho_G / \rho_L)^{1/2} \quad (15)$$

where:

L = liquid flow, kg/s

G = vapor flow, kg/s

The liquid phase capacity factor, c_L, is defined by:

$$c_L = V_L\,(\rho_L / (\rho_L - \rho_G))^{1/2} \quad (16)$$

where:

V_L = superficial liquid velocity, m/s

c_L is related to the vapor capacity factor by:

$$c_G^{1/2} + m(c_L)^{1/2} = n \quad (17)$$

where:

m and n are constants.

The straight line correlations given in (17) were obtained for two separate hydraulic regimes:

Low liquid loads, $(c_L)1/2 < 0.07$ (m/s)$^{1/2}$

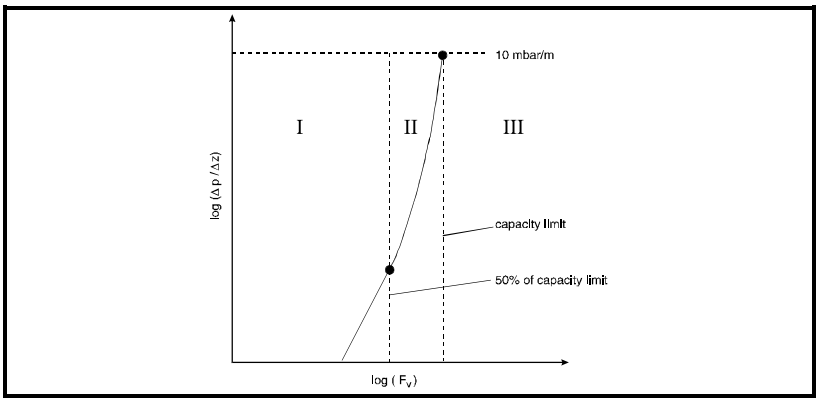
High liquid loads, $(c_L)1/2 > 0.07$ (m/s)$^{1/2}$

The capacity correlations have been shown to predict the column capacity within an accuracy of 6%.

Pressure Drop

The pressure drop model used in PRO/II for structured packings is a sum of three separate correlations as shown in Figure 2.4.3-1.

Figure 2.4.3-1: Pressure Drop Model



The F-factor in Figure 2.4.3-1 is defined as:

$$F\text{–}factor = V_G(\rho_G)^{1/2} \qquad (18)$$

Region I is for columns operating below 50% capacity. In this region the wetted wall column model is used to obtain a straight-line relationship between the logarithm of the pressure drop and the logarithm of the F-factor. At the end of region II (and the beginning of region III), where the capacity limit is reached, the pressure drop is obtained from the capacity correlation. Finally, the correlation in region II is modeled by using a quadratic polynomial to join regions I and III. At the juncture of regions I and II, the polynomial approximation has the same slope as the wetted wall correlation in region I. It should be noted that the pressure drop correlations for all Sulzer packing types were developed without considering the liquid viscosity.

Efficiency

The column efficiency or separation performance for Sulzer packing is measured by the number of theoretical stages per meter (NTSM). The NTSM is therefore the inverse of the height equivalent of a theoretical plate (HETP). The NTSM is defined as:

$$NTSM = Sh_G D_G a_I / d_h V_G \qquad (19)$$

where:

Sh_G = Sherwood number of the vapor phase = $k_G d_h / D_G$

D_G = diffusion coefficient of the vapor phase

a_I = interfacial area per unit volume of packing, m^2/m^3

d_h = hydraulic diameter of packing, m

k_G = vapor phase mass transfer coefficient

The mass transfer in Sulzer packings has been modeled by neglecting the liquid phase mass transfer coefficient, k_L. This was done because the value of the vapor phase mass transfer coefficient, k_G, is most often much less numerically than k_L. Experimental data were used to obtain the following relationship for the Sherwood number:

$$Sh_G = \mathrm{Re}_G^m \, Sc_G^{1/3} \qquad (20)$$

The relationship for the interfacial area is given by:

$$a_I = (\rho_L \, V_L)^{0.2} \qquad (21)$$

For metal packing types such as the MELLAPAK series, the factor m in equation (20) usually has a value of 0.8. For gauze packings such as BX or CY, the factor m has a value closer to 1, i.e., independent of the liquid load. This is because gauze packings are more completely wetted, regardless of the liquid load, while for metal packings the wetted area increases with increasing liquid load. The NTSM correlations are obtained by substituting equations (20) and (21) into equation (19).

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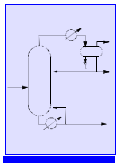


2.4.4 Shortcut Distillation

General Information

PRO/II contains shortcut distillation calculation methods for determining column conditions such as separations, minimum trays, and minimum reflux ratios. The shortcut method assumes that an *average* relative volatility may be defined for the column. The Fenske method is used to compute the separations and minimum number of trays required. The minimum reflux ratio is determined by the Underwood method. The Gilliland method is used to calculate the number of theoretical trays required and the actual reflux rates and condenser and reboiler duties for a given set of actual to minimum reflux ratios. Finally, the Kirkbride method is used to determine the optimum feed location.

The shortcut distillation model is a useful tool for preliminary design when properly applied. Shortcut methods will not, however, work for all systems. For highly non-ideal systems, shortcut methods may give very poor results, or no results at all. In particular, for columns in which the relative volatilities vary greatly, shortcut methods will give poor results since both the Fenske and Underwood methods assume that one average relative volatility may be used for calculations for each component.

Fenske Method

The relative volatility between components i and j at each tray in the column, is equal to the ratio of their K-values at that tray, i.e.:

$$\alpha_{ij}^{N} = \frac{y_i^N / x_i^N}{y_j^N / x_j^N} = \frac{K_i^N}{K_j^N} \qquad (1)$$

where:

y = mole fraction in the vapor phase

x = mole fraction in the liquid phase

subscripts i, j refer to components i and j respectively

superscript N refers to tray N

For small variations in volatility throughout the column, an average volatility, may be defined. This is taken as the geometric average of the values for the overhead and bottoms products:

$$\alpha_{ij}^{av} = \sqrt{\alpha_{ij}^{1}\,\alpha_{ij}^{N}} \qquad (2)$$

The minimum number of theoretical stages is then given by:

$$N_{\min} = \frac{\log \frac{x_{i,D}}{x_{j,D}} \frac{x_{j,B}}{x_{i,B}}}{\log \alpha_{ij}^{av}} \quad (3)$$

where:

subscripts *B,D* refer to the bottoms and distillate respectively

Underwood Method

The values of the relative volatilities of the feed components determine which components are the light and heavy key components. The light key component for a feed of equivalent component concentrations is usually the most volatile component. For a feed where some components are found in very small concentrations, the light key component is the most volatile one found at important concentrations. The heavy key component is similarly found to be the least volatile component, or the least volatile component found at significant concentrations.

The relative volatility of each component can therefore be expressed in terms of the volatility of the heavy key, i.e.,

$$\alpha_J = \frac{K_j}{K_{hk}} \quad (4)$$

where:

J refers to any component, and hk refers to the heavy key component

For components lighter that the heavy key, $\alpha_J > 1$, and for components heavier than the heavy key, $\alpha_J < 1$. for the heavy key component itself, $\alpha_J = 1$.

The Underwood method is used to determine the reflux ratio requiring an infinite number of trays to separate the key components. For a column with infinite trays, the distillate will exclude all components heavier than the heavy key component. Similarly, the bottoms product will exclude all components lighter than the light key. Components whose volatilities lie between the heavy and light keys will distribute between the distillate and bottoms products. An equation developed by Shiras *et al*. can be used to determine if the selected keys are correct. At minimum reflux ratio:

$$\frac{x_{J,D}D}{x_{J,F}F} = \frac{\alpha_J - 1}{\alpha_{lk} - 1}\frac{x_{lk,D}D}{x_{lk,F}F} + \frac{\alpha_{lk} - \alpha_J}{\alpha_{lk} - 1}\frac{x_{hk,D}D}{x_{hk,F}F} \quad (5)$$

If the value of the ratio given by equation (5) is less than -0.01 or greater than 1.01 for any component J, then that component will likely not distribute between both products. Therefore to test if the correct key components are selected, equation (5) should be applied to those components lighter than the light key, and heavier than the heavy key. If they fail the test described above, then new key components should be selected.

It should be noted that an exact value of R_{min} is not needed. This value is necessary only to provide an estimate of the product composition, and to determine if the specified reflux ratio is reasonable. The Underwood equations assume a constant relative volatility, as well as a constant liquid/vapor rate ratio throughout the column. The first equation to be solved is:

$$(1-q) = \sum_{i=1}^{N} \frac{\alpha_J x_{J,F}}{\alpha_J - \phi} \qquad (6)$$

$$q = \frac{H_G - H_F}{H_v} \qquad (7)$$

where:

q = thermal condition of feed
= heat to convert to saturated vapor/heat of vaporization
H_G = molar enthalpy of feed as a saturated vapor
H_F = molar enthalpy of feed
H_v = molar latent heat of vaporization
$x_{J,F}$ = mole fraction of component J in feed
ϕ = a value between the relative volatilities of the light and heavy keys, i.e., α_{hk} (=1) < ϕ < α_{lk}

The second equation to be solved is:

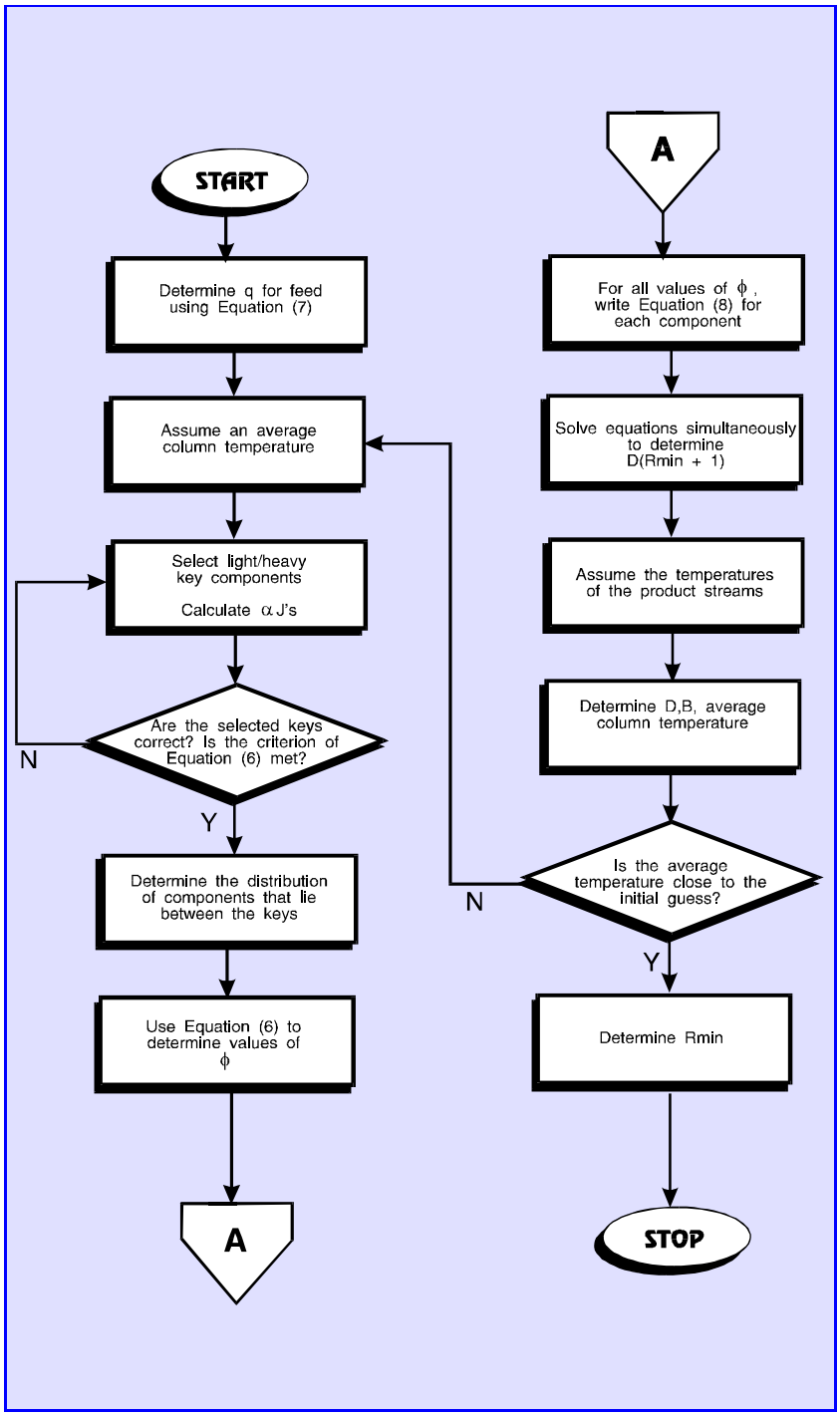
$$(R_{min} + 1) = \sum_{i=1}^{N} \frac{\alpha_J x_{J,D}}{\alpha_J - \phi} \qquad (8)$$

where:

R_{min} = minimum reflux ratio = $(L/D)_{min}$
$x_{J,D}$ = mole fraction of component J in distillate

The algorithm used to solve for R_{min} is given in Figure 2.4.4-1.

Figure 2.4.4-1: Algorithm to Determine R_{min}


START
Determine q for feed using Equation (7)
Assume an average column temperature
Select light/heavy key components
Calculate α J's
Are the selected keys correct? Is the criterion of Equation (6) met?
N
Y
Determine the distribution of components that lie between the keys
Use Equation (6) to determine values of ϕ
A
A
For all values of ϕ, write Equation (8) for each component
Solve equations simultaneously to determine D(Rmin + 1)
Assume the temperatures of the product streams
Determine D,B, average column temperature
Is the average temperature close to the initial guess?
N
Y
Determine Rmin
STOP

Kirkbride Method

The optimum feed tray location is obtained from the Kirkbride equation:

$$\log\left[\frac{m}{p}\right] = 0.206 \log\left\{\frac{B}{D}\frac{x_{hk,F}}{x_{lk,F}}\left(\frac{x_{lk,B}}{x_{hk,D}}\right)^2\right\} \quad (9)$$

where:

m = number of theoretical stages above the feed tray

p = number of theoretical stages below the feed tray

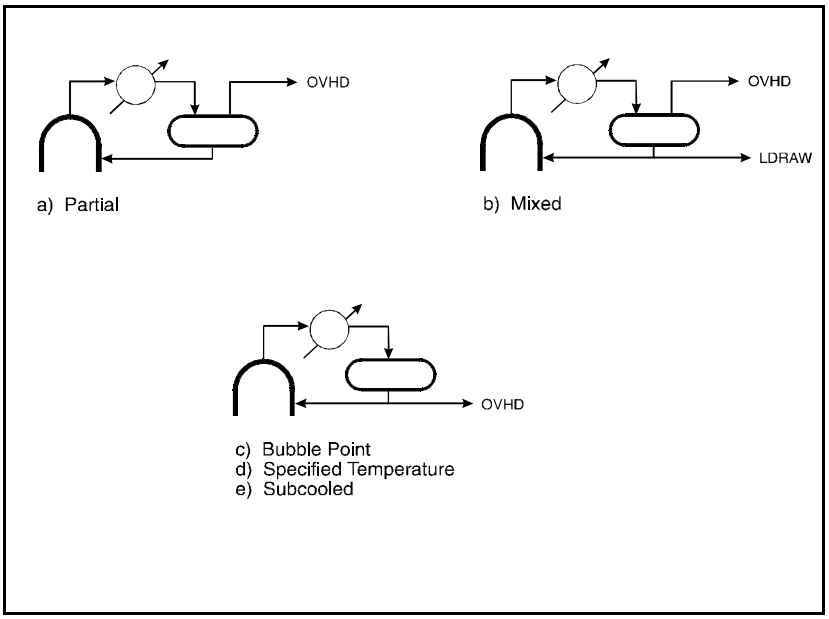
Gilliland Correlation

The Gilliland correlation is used by PRO/II to predict the relationship of minimum trays and minimum reflux to actual reflux and corresponding theoretical trays.

The operating point selected by the user (expressed as either fraction of minimum reflux or fraction of minimum trays) is selected as the mid-point for a table of trays and reflux. Based on the corresponding reflux ratio, the column top conditions are calculated and the associated condenser duty determined.

The reboiler load is computed from a heat balance. Note that the selection of the proper condenser type is vital to accurate calculation of heat duties. Also, the condenser type selected will have no effect whatsoever on the separations predicted. Figure 2.4.4-2 shows the condenser types available in PRO/II for the shortcut distillation model. Water may be decanted at the condenser.

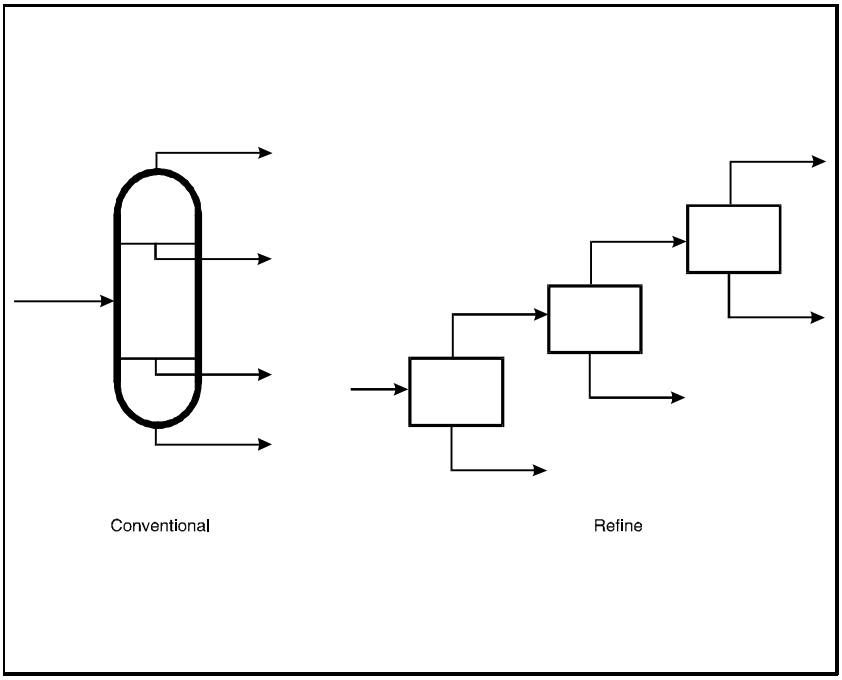
Figure 2.4.4-2: Shortcut Distillation Column Condenser Types



Distillation Models

There are two shortcut distillation models available in PRO/II, as shown in Figure 2.4.4-3. In the first method (CONVENTIONAL), which is the default, total reflux conditions exists in the column. In the second method (REFINE), the shortcut column consists of a series of one feed, two product columns, starting with the bottom section. In this model, there is no reflux between the sections.

Figure 2.4.4-3: Shortcut Distillation Column Models



Simple Columns

Simple columns are defined a columns in which a single feed location may be defined, located somewhere between the reboiler and condenser. Obviously, absorbers and strippers do not meet these criteria and it is recommended that only the rigorous distillation method (see Section 2.4.1, *Rigorous Distillation Algorithms*) be used for these types of columns.

Moreover, it is not possible to predict extractive distillation or any separation in which K-values vary widely with composition, since such columns violate the Fenske and Underwood assumptions. For example, calculation of the stages and reflux for a propylene-propane splitter by shortcut methods will give very poor results since for this type of column the relative volatility varies from 1.25 in the reboiler to 1.07 in the condenser. Thus, the Fenske method will greatly under-predict the minimum trays required and the Underwood method will under-predict the minimum reflux required for the separation.

For simple columns, in which the relative volatilities do not vary greatly and in which equal molal overflow is approached, the shortcut calculations allow bracketing a reasonable design base.

An operating point expressed as either fraction of minimum reflux or trays may be selected by the user. This is a design parameter and usually a matter of personal preference or company standards. However, a value of 1.5 times minimum reflux or two times minimum trays will usually give a reasonable basis for a simple column.

Selection of the separation key components is a primary importance for the Underwood method. It is extremely important that the light and heavy keys be distributed in both products, with their distribution defining a sharp separation. This may mean that the keys must be ‘‘split’’, with middle component(s) which distribute loosely in both products allowed to float as required to meet the sharp separation of the keys. Incorrect selection of keys can give poor and meaningless results, moreover, this can result in failure of the Underwood calculations. As a general rule of thumb, the more nonideal a column, the more the Underwood method will under-predict the reflux requirements.

The column heat requirements will be predicted based on the condenser type selected. For subcooled condensers, it is necessary to define the temperature to insure that the subcooling effect is considered.

For type 2 condensers (mixed-phase) the separation into vapor and liquid products should not be attempted in the shortcut model, since this would require two specifications (for a flash drum). Separation into liquid and vapor products is accomplished by sending the shortcut overhead product (mixed-phased) to an equilibrium flash drum calculation. When the column overhead is known to contain water, it is important that the estimated overhead product rate include both water and hydrocarbon product.

While any type of product specification may be used to define the split, the Underwood calculations will only be useful when the specifications describe a sharp split between a light and heavy key. If the number of Fenske trays (fractionation index) is given in lieu of a specification, this may also invalidate the Underwood calculations.

If desired, the user may supply estimates of the Fenske trays required for the separation. For columns in which there are a large number of trays, this will speed convergence.

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PRO/II Note: For more information on supplying estimates of the number of Fenske trays using the FINDEX keyword, see Section 78, *Shortcut Distillation*, of the *PRO/II Keyword Input Manual*.

Complex Columns

For complex columns (in which there are more than two products) it becomes impossible to select key components to define the fractionation within the various sections. For such columns, the separation is defined indirectly in terms of stream properties. The PRO/II program allows a wide variety of such properties.

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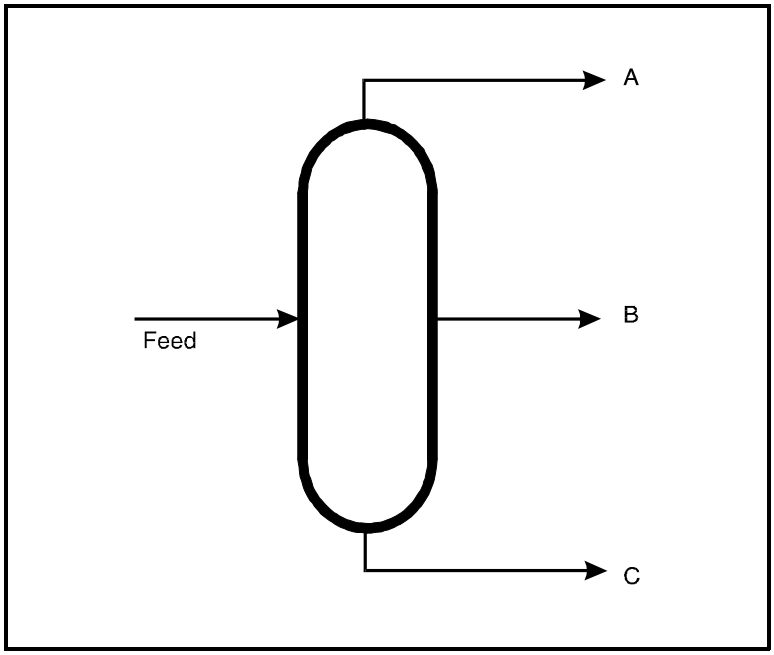
PRO/II Note: For a list of stream properties which may be defined in the shortcut distillation column, see Table 43.2A in Section 43, *Flowsheet Parameters*, of the *PRO/II Keyword Input Manual*.

As mentioned above, two models are available for complex columns. For the CONVENTIONAL model, Fenske relationships defining the column sections (each section having two products) are solved simultaneously, thus the interaction of reflux between the sections is considered. For the REFINE model, each section is solved independently, starting from the bottom. This model closely approximates typical oil refinery columns in which total liquid draws are sent to side strippers and little (if any) liquid is returned to the next lower tray.

As the number of products increases, the difficulty in definition of nonconflicting specifications also increases. There are often upper and lower limits for each specification. For example, the total product rate cannot exceed the feed rate. Furthermore, for specifications such as ASTM/TBP temperatures, the selection of the components to represent the feed streams can be very important. For example, it would not be reasonable to attempt to separate ten components into six products, etc. Care should be exercised that the specifications define rates for all products (either directly or indirectly). For illustration, consider the following example shown in Figure 2.4.4-4:

Figure 2.4.4-4: Shortcut Column Specification



For this column, four specifications are required. Selection of two specifications each for products A and C would satisfy this requirement, however, it might not be sufficient to define stream B. Therefore, a better set of specifications would include values for all the products, A, B and C. As a general rule, it is best that specifications omissions be limited to the top stream.

Specifications may be grouped into two general categories:

- Bulk properties: Gravities, Rates (mole, volume, weight)
- Intensive properties: ASTM/TMP Distillations, Component rates/ purities, Special properties

As a general rule, fractionation indices may be defined in conjunction with bulk properties, but will not work well when used with intensive properties. For intensive properties, the additional flexibility of allowing PRO/II to calculate the Fenske trays is highly desirable.

The nature of the Fenske calculations necessitates judgment when using specifications such as ASTM/TBP distillation points. End points and initial points may be distorted by the Fenske model because of the infinite reflux assumption, resulting in ‘‘trimming’’ of the stream tails (initial points too high, end points too low). Moreover, the component selection may also greatly affect the initial and end points. For these reasons, it is recommended the 5% and 95% points be chosen in lieu of initial and end points.

Refinery Heavy Ends Columns

The second model is extremely useful for prediction of yields and analyzing data for crude units, vacuum units, cat fractionators, bubble towers, etc. There are generally two possible situations when dealing with such columns:

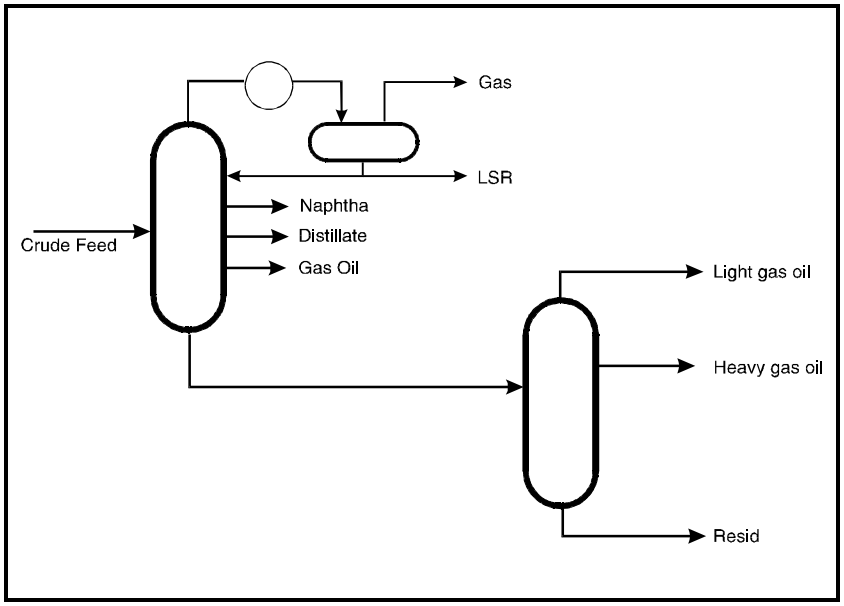
a) Yields are to be predicted, based on a given feed composition.

b) Operating data are to be checked by comparison of the predicted product properties with the actual product properties. The operating product rates are used for this case.

The selection of components cannot be over-emphasized for such studies. While minimization of component numbers is desirable for simulation cost reduction, sufficient components must be included to enable accurate simulation. In particular, for case a), the yields predicted can be greatly influenced by the components chosen. For case b), it is a relatively simple matter to adjust the components used as required to more accurately predict product properties. For case a), this a more complex task with judgment necessarily applied in light of the simulation requirements. The standard cuts used by PRO/II have been developed for crude unit simulation and will give good results. It is generally recommended that compromises to the standard cuts be made in the heavier components (above 800 F) where possible.

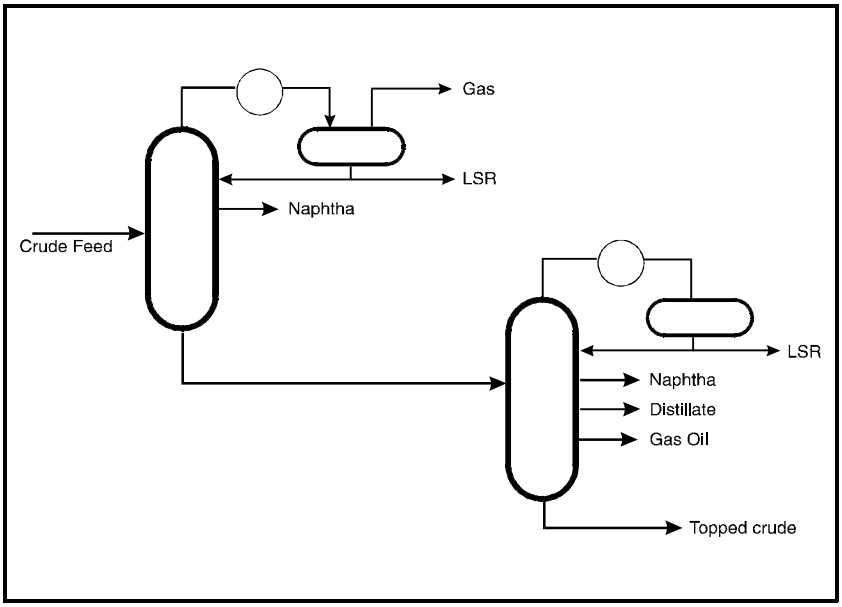
For series of columns, the shortcut model itself can be important. For the crude-vacuum unit combination shown in Figure 2.4.4-5, the system may be simulated as one column or two. It is usually better to use two shortcuts, since the crude unit products will be well defined while the vacuum products may be somewhat nebulous. In this way, the crude unit yields will not be affected by errors in definition of the vacuum unit yields and bulk properties may then be described for the vacuum unit to aid solution. On the other hand, if definitive vacuum product specifications are available, the single unit model can insure more accurate vacuum unit yields.

Figure 2.4.4-5: Heavy Ends Column



The crude-preflash system shown in Figure 2.4.4-6 presents a different case.

Figure 2.4.4-6: Crude-Preflash System



For this case, common products will be produced on both units and a single column model attempting to represent all the products is difficult (if not impossible). For systems such as this it is much better to always use a two column model.

The sections in actual distillation columns are interlinked through both feeds and liquid refluxes. Refluxes at each section are governed by heat balances around that section and the entire system. Although some adjustment in reflux is possible, there is an upper limit to the number of trays which can be present in any section. For a crude column, this is usually around 6 to 8 theoretical trays. This is because the heavy-end mixtures have wide boiling ranges. Once the product rates are fixed, each mixture can only have limited bubble point ranges. In other words, the fractionation within each section is restricted and depends to a large extent on the overall heat balance.

The Fenske model is useful in defining the fractionation requirements within each section. While the fractionation index (Fenske trays) is only qualitatively definitive, it is useful in evaluating the feasibility of desired separation.

The fractionation index is approximately equivalent to the number of theoretical trays times the reflux ratio; thus, the theoretical stages required for a given separation may be estimated. (These trays must then be adjusted accordingly to correspond to actual trays).

Experience has shown that the fractionation indices fall into certain ranges for refinery columns. Table 2.4.4-1 below illustrates typical values:

Table 2.4.4-1: Typical Values of FINDEX

Crude	Typical FINDEX
LSR - Naphtha	5 - 7
Naphtha - Kero	4 - 5
Kero - Diesel	2.5 - 3.5
Diesel - Gas Oil	2 - 2.5
Gas Oil - Topped Crude	1.25 - 1.75
Cat Fractionators	
Gasoline - Light Cycle	5 - 7
Light Cycle - Heavy Cycle	1.5 - 2.5
Heavy Cycle - Clarified Oil	1.1 - 1.5
Vacuum Units	
Overhead - Light Gas Oil	2 - 2.5
Light Gas Oil - Heavy Gas Oil	1.25 - 1.75
Heavy Gas Oil - Resid	1 - 1.5

Values of fractionation indices differing greatly from the above values suggest impossibilities or conflicts in the product specifications used for the model.

When it is desired to use the shortcut model to verify yields and properties, it is suggested that the product yields and/or gravities be used in conjunction with the typical fractionation induces shown above. It is interesting to note that values selected anywhere within the ranges given will produce nearly identical products. This also illustrates rather graphically the controlling effect of product draw rate versus trays for such columns.

When using the shortcut model for rate prediction it is recommended that fractionation indices not be used in conjunction with intensive properties. Definition of the fractionation with FINDEX may very well result in a case that is impossible to converge.

For yield prediction, a combination of product ASTM 95% temperatures and gaps works very well for crude units. For the topped crude, a gap of 100 to -150 °F with the gas oil usually gives a reasonable operation, or the gravity of the topped crude may also be used for a specification.

Troubleshooting

Simple Columns

Simple columns are defined as consisting of one feed and two products, with reboilers and condensers. Systems with two overhead products (partial condensers) are simulated with one combined overhead product, with the separation to vapor and liquid products being accomplished in an ensuing flash drum.

Troubleshooting is usually simple for such columns. Fenske calculation failures are usually caused by:

- Impossible or conflicting specifications which result in impossible material balances. (In particular, look for this situation when component mole fractions are specified).
- User specified fractionation index (minimum Fenske trays) for which it is impossible to meet other specifications.
- Poor product rate estimates – in particular, caused by not accounting for water in the top product.

Underwood calculation failures are caused by incorrect separation key selection. Possible causes are:

- Heavy and light key components which both distribute to the same product.
- Heavy and light key components which do not define a sharp separation. (For this case ‘‘split’’ keys must be defined.)

Note: The trial calculations for the shortcut fractionator will be printed when a PRINT statement with the keyword TRIAL is included in the SHORTCUT unit operation. This may be used to help diagnose Fenske failures.

Complex Columns

For complex columns (more than two products), a series of two product columns are used to represent the separations with the feed introduced into the bottom section. The default model type one considers the effect of reflux between the sections; model two assumes to reflux between the sections. The second model type is very useful for simulation of petroleum refinery ‘‘heavy ends’’ columns.

For these columns, it is impossible to select key components to define the fractionation within the various sections. Therefore, the separations must be indirectly defined using product stream properties. As the number of products increase, it becomes increasingly difficult to define non-conflicting product specifications. There are also usually upper and lower limits for each specification based on material balance considerations and feed representation. Care must be exercised to define specifications which result in unique rates for all products (either directly or indirectly).

Calculation failures are always related to specifications. Some possible problems include:

- Conflict of fractionation indices with intensive stream property specifications. In general, this combination of specifications should be avoided and fractionation index used only in conjunction with stream bulk properties such as rates and gravities.
- Specifications which do not result in a unique rate for each product stream.
- Component definition which does not allow the desired separations to be accomplished (either too few components or incorrect component boiling point ranges).
- Distortion of ASTM/TBP initial and endpoints by the Fenske model because of the infinite reflux assumption. (5% and 95% specifications are much better than initial and endpoint specifications.)

Since the solution of the entire system of two product sections is iterative and simultaneous, it is possible that a poor specification in one section may result in a seeming problem for another section. Usually there is a single specification which ‘‘binds’’ the system and prevents solution.

Inspection of the trial calculated results will often reveal the interactions of the specifications, and hence, the incompatibility. For petroleum refinery ‘‘heavy ends’’ calculations, the predicted fractionation indices may be evaluated in the light of typical values for such columns. (See Table 2.4.4-1.)

Examination of the component distribution to the various product streams in the stream printout is useful for checking the component definition for ‘‘reasonableness’’. For the most accurate simulation of crude units, the standard cut ranges should be used. Cut ranges may be broadened to reduce the simulation cost, however, Table 2.4.4-2 illustrates the effect of changing the cut ranges on the product yields for a typical crude unit.

Table 2.4.4-2:
Effect of Cut Ranges on Crude Unit Yields Incremental Yields from Base

Product	Base Case* Bbls/Day	Case 1 % Increase	Case 2 % Increase	Case 3 % Increase	Case 4 % Increase	Case 5 % Increase
Overhead	23159	-2.4	-0.3	-	-	-
Naphtha	23285	+6.2	+0.4	-0.3	-	-
Kerosene	16232	-8.2	+0.3	+1.7	-	+0.7
Diesel	19149	-0.2	-0.6	-0.2	+0.9	-2.1
Gas Oil	11002	+11.2	-15.4	-16.5	-16.9	-6.4
Topped Crude	42173	1.8	+3.6	+3.8	+4.0	+2.3
Total	135000					
No. Comps	46	36	49	45	39	37
No. of Cuts						
100-600	-	-	-	-	-	20
600-800	-	-	-	-	-	5
100-800	28	15	38	34	28	-
800-1200	8	-	4	4	4	5
800-1500	-	15	-	-	-	-
1000-1500	-	-	1	1	1	-
1200-1500	4	-	-	-	-	1

Note: For all cases, yields were predicted, based on product 95% points and 5-95 gaps.

* Standard cuts

It is recommended that a systematic approach be taken when debugging shortcut columns. Trial printouts will often reveal clues to the limiting specification. Increasing the number of calculation trials is never a good strategy, since solution will normally be reached well within the default number of trials (20).

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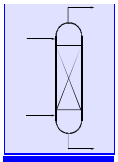


2.4.5 Liquid-Liquid Extractor

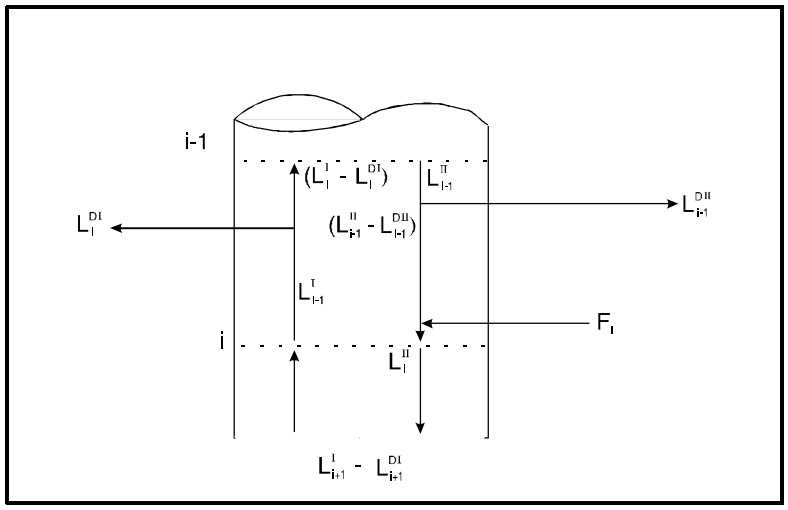
General Information

Liquid-liquid extractions are modeled in PRO/II using the general trayed column model in conjunction with the LLEX algorithm. The LLEX algorithm in PRO/II is a Newton based method which is suited to solving non-ideal distillation problems involving a smaller number (10 vs. 100) of chemical species. LLEX is designed to solve liquid-liquid equilibrium problems with more than one equlibrium stage.

Basic Algorithm

Figure 2.4.5-1 shows a schematic of an equilibrium stage with a lighter liquid (denoted as liquid-1) and a heavier liquid (liquid-2) in equilibrium.

Figure 2.4.5-1: Schematic of a Simple Stage for LLEX



The equations which describe the interior trays of the column are as follows (with all rates, compositions, and enthalpies expressed on a molar basis):

Component Mass Balance Equations:

$$M_{i,j} = \exp\left(X_{ij}^{I}\right)L_i^{I} + \exp\left(X_{ij}^{II}\right)L_i^{II} - \exp\left(X_{i-1,j}^{II}\right)\left(L_{i-1}^{II} - L_{i-1}^{DII}\right) - \exp\left(X_{i+1,j}\right)\left(L_{i+1,j}^{I}\right) - F_{i,j} \qquad i=1, NT \tag{1}$$

Energy Balance Equation:

$$E_i = L_i^{I} H_i^{I} + L_i^{II} H_i^{II} - \left(L_{i-1}^{II} - L_{i-1}^{DII}\right)H_{i-1}^{II} - \left(L_{i+1}^{I} - L_{i+1}^{DI}\right)H_{i+1}^{I} - Q_i - F_i H_i \qquad i=1, NT \tag{2}$$

Liquid-Liquid Equilibrium Equations:

$$LLE_{i,j} = X^{I}_{i,j} - X^{II}_{i,j} - ln(K_{i,j)} \qquad i = 1,NT \text{ and } j = 1,NC \qquad (3)$$

Summation of Mole Fractions:

$$S_i = 1 - \sum \exp\left(X^{I}_{i,j}\right) \qquad i = 1,NT \qquad (4)$$

$$S'_i = 1 - \sum \exp\left(X^{II}_{i,j}\right) \qquad i = 1,NT \qquad (5)$$

where:

F_i =	total feed flow to tray i
L^{I}_i =	total liquid-1 flow from tray i
L^{II}_i =	total liquid-2 flow from tray i
Q_i =	heat added to tray i
T_i =	temperatures of tray i
$X^{I}_{i,j}=\ln(x^{I}_{i,j})$ =	natural log of the liquid-1 mole fractions
$X^{II}_{i,j}=\ln(x^{II}_{i,j})$ =	natural log of the liquid-2 mole fractions
$K_{i,j}$ =	liquid-liquid equilibrium constant for component j, on tray i
NC =	number of components
NT =	number of trays

subscripts:

i	refers to the tray index
j	refers to the component index

superscripts:

D =	refers to a draw
L =	refers to a liquid-1 property
L =	refers to a liquid-2 property
I =	refers to a liquid-1 phase
II =	refers to a liquid-2 phase

The unknowns, alternatively referred to as iteration or primitive variables:

$$(\underline{X}^{I} , \underline{X}^{II} , L^{I} , L^{II} , T)_i \text{ , where i = 1,NT}$$

are solved for directly using an augmented Newton-Raphson method. Specification equations involving the iteration variables are added directly to the above equations and solved simultaneously.

The modifications of the Newton-Raphson method are twofold. The first is a line search procedure that will, when possible, decrease the sum of the errors along the Newton correction. If this is not possible, the size of the increase will be limited to a prescribed amount.

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PRO/II Note: See Section 70, *Column Input*, in the *PRO/II Keyword Input Manual* for more information.

The second modification limits the changes in the individual iteration variables. Both of these modifications can result in a fractional step in the Newton direction. The fractional step size, α, is reported in the iteration summary of the LLEX output.

Note: An α of 1 indicates that the solution procedure is progressing well and that, as the solution is approached, α should become one.

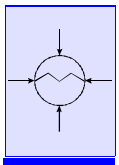
For highly non-linear systems which may oscillate, the user can restrict the step size by specifying a damping factor which reduces the changes in the composition variables. A cutoff value is used by the algorithm so that when the value of the sum of the errors drops below the given level, the full Newton correction is used. This serves to speed the final convergence.

The iteration history also reports the largest errors in the mass balance , the energy balance, and the liquid-liquid equilibrium equations. Given a good initial estimate, these should decrease from iteration to iteration. However, for some systems, the errors will temporarily increase before decreasing on the way to finding a solution. The keyword ERRINC limits the size of the increase in the sum of the errors.

All derivatives for the Jacobian matrix are calculated analytically. User-added thermodynamic options that are used by LLEX must provide partial derivatives with respect to component mole fractions and temperature. LLEX uses the chain rule to convert these to the needed form.

References

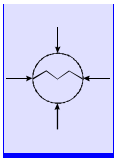
1. Bondy, R.W., *A New Distillation Algorithm for Non-Ideal System*, paper presented at AIChE 1990 Annual Meeting.
2. Shah, V.B., and Kovach, J.W. III, Bluck, D., *A Structural Approach to Solving Multistage Separations, paper presented at 1994 AIChE Spring meeting.*



2.5 Heat Exchangers

Process heat transfer equipment may be simulated in PRO/II using one of three heat exchanger models:

- Simple heat exchanger
- Rigorous heat exchanger
- Liquified Natural Gas (LNG) heat exchanger



2.5.1 Simple Heat Exchangers

General Information

Heat exchangers are used to transfer heat between two process streams, or between a process stream and a utility stream such as air or steam. For all three heat exchanger models, the following basic design equation holds:

$$\delta q = U_o \Delta T \delta A \qquad (1)$$

where:

δq = heat transferred in elemental length of exchanger dz

U_o = overall heat transfer coefficient

ΔT = overall bulk temperature difference between the two streams

δA = element of surface area in exchanger length dz

Once an appropriate mean heat-transfer coefficient, and temperature difference is defined, equation (1) may be re-written for the entire exchanger as follows:

$$Q = U_{om} A_o \Delta T_m = H_{out} - H_{in} \qquad (2)$$

where:

Q = total exchanger heat duty

U_{om} = overall mean heat-transfer coefficient

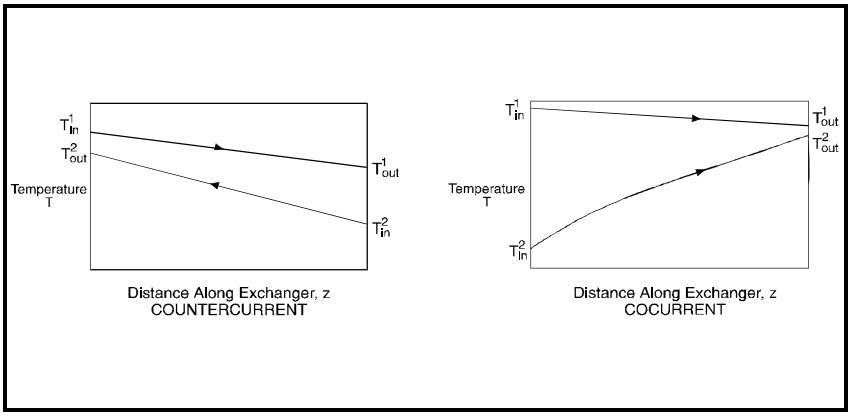
A_o = total exchanger area

ΔT_m = mean temperature difference

Calculation Methods

The simple heat exchanger model in PRO/II may be used to simulate heat exchange between two process streams, heat exchange between a process stream and a utility stream, or to heat or cool a single process stream. The simple model does not rigorously rate the exchanger, i.e., pressure drops, shell and tubeside heat transfer coefficients, fouling factors are not calculated.

Figure 2.5.1-1: Heat Exchanger Temperature Profiles



For countercurrent or cocurrent flows as shown in Figure 2.5.1-1, the appropriate expression for the mean temperature difference is the logarithmic mean, i.e.:

For countercurrent flows,

$$\Delta T_{lm} = LMTD = \frac{\left(T^1_{in} - T^2_{out}\right) - \left(T^1_{out} - T^2_{in}\right)}{\ln\left[\frac{T^1_{in} - T^2_{out}}{T^1_{out} - T^2_{in}}\right]} \quad (3)$$

For cocurrent flows,

$$\Delta T_{lm} = LMTD = \frac{\left(T^1_{in} - T^2_{in}\right) - \left(T^1_{out} - T^2_{out}\right)}{\ln\left[\frac{T^1_{in} - T^2_{in}}{T^1_{out} - T^2_{out}}\right]} \quad (4)$$

where:

ΔT_{lm} = LMTD = logarithmic mean temperature difference

superscript *1* denotes one side of the heat exchanger

superscript *2* denotes the other side of the heat exchanger

In actual fact, the flows are not generally ideally countercurrent or cocurrent. The flow patterns are usually mixed as a result of flow reversals (e.g., in exchangers with more than one tube or shell pass), bypassed streams, or streams which are not well mixed. F-factors have been derived by Bowman *et al.* to account for these non-ideal flow patterns and are used in PRO/II to correct equations (3) and (4). For multipass heat exchangers, where the ratio of shell passes to tube passes given is not 1:2 (e.g., for a 2 shell- and 6 tubepass exchanger), the F-factors actually used are those computed for exchangers with the ratio of one shell to two tubepasses (i.e., for 2 shell- and 4 tubepasses).

The method used by PRO/II to determine the heat transferred when using utility streams is given by:

- For water and air cooling utility streams, the only heat transfer considered is sensible heat, i.e.,

$$Q = \left(H_{out} - H_{in}\right)_{w,a} = hA\left(T_{out} - T_{in}\right) \qquad (5)$$

where:

h = sensible heat transfer coefficient

H = enthalpy of utility stream

- For steam or refrigerant utilities, only latent heat is considered in the heat transfer. Either the saturation temperature (T_{sat}) or saturation pressure (P_{sat}) must be supplied.

$$Q = m\lambda \qquad (6)$$

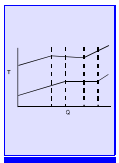
where:

m = mass flowrate of utility stream

λ = latent heat at T_{sat}

Any one of the following specifications may be made in PRO/II:

- Overall exchanger heat duty
- Product stream temperature (hot or cold side)
- Product stream liquid fraction (hot or cold side)
- Product stream temperature approach to the bubble or dew point (hot and cold side)
- Hot side outlet to cold side inlet temperature approach
- Hot side inlet to cold side outlet temperature approach
- Hot side outlet to cold side outlet temperature approach
- Minimum internal temperature approach
- Overall heat transfer coefficient (U) and area (A) given



2.5.2 Zones Analysis

General Information

Conventionally for a simple heat exchanger, the logarithmic mean temperature difference is calculated using the stream temperatures at the inlet and outlet of the unit (equations (3) and (4) in the previous section 2.5.1, *Simple Heat Exchangers*). Optionally, PRO/II can compute a duty-averaged LMTD. This option becomes increasingly useful when phase changes occur along the length of the exchanger. Under these conditions, the LMTD calculated as described for the simple heat exchanger may often be inadequate because of the non-linearity of the enthalpy-temperature characteristics of the stream changing phase. Zone analysis may therefore be extremely useful for locating internal temperature pinches.

Calculation Methods

In this method, the heat exchanger is divided into a number of *zones*, and the heat exchanger design equation is then applied to each zone separately. The number of zones may be specified by the user, or be automatically selected by PRO/II. Automatic selection by PRO/II ensures that all the phase changes are located on the zone boundaries. No zone should account for more than 20% of the total heat exchanger duty; therefore, a minimum of 5 zones is required. PRO/II may use up to a maximum of 25 zones.

The design equation for the heat exchanger is given by:

$$Q = U_{om} A_o LMTD_{zones} = H_{out} - H_{in} \qquad (1)$$

For a total of n zones, $LMTD_{zones}$ is calculated from the individual zones values as a weighted LMTD:

$$LMTD_{zones} = \frac{Q}{\sum_{i=1}^{n} \frac{Q_i}{LMTD_i}} \qquad (2)$$

where:

Q = total exchanger duty

Q_i = heat duty in zone i

$LMTD_i$ = logarithmic mean temperature difference for zone i

The LMTD values for the individual zones are computed using the temperatures of the streams entering and leaving each zone.

For countercurrent flows in zone i,

$$LMTD_i = \frac{\left(T^1_{in,i} - T^2_{out,i}\right) - \left(T^1_{out,i} - T^2_{in,i}\right)}{\ln\left[\frac{T^1_{in,i} - T^2_{out,i}}{T^1_{out,i} - T^2_{in,i}}\right]} \quad (3)$$

For cocurrent flows in zone i,

$$LMTD_i = \frac{\left(T^1_{in,i} - T^2_{in,i}\right) - \left(T^1_{out,i} - T^2_{out,i}\right)}{\ln\left[\frac{T^1_{in,i} - T^2_{in,i}}{T^1_{out,i} - T^2_{out,i}}\right]} \quad (4)$$

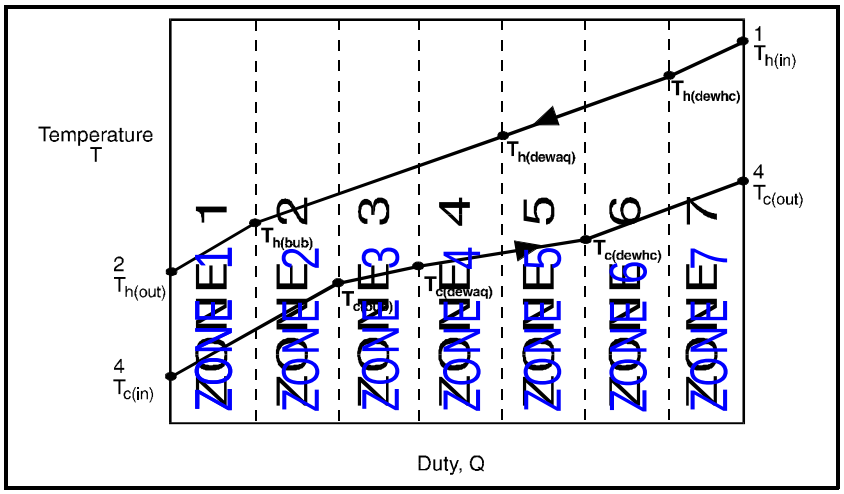
For all the heat exchanger specifications described above, except for the minimum internal temperature approach, the zones analysis is independent of the calculation of the overall heat duty. In these cases, by default, the $LTMD_{zones}$ value is calculated and reported after the equations for the exchanger have been solved, but is not used in heat transfer calculations. The user may, however, specify that the zones analysis be done at calculation time, i.e., while PRO/II is solving the design equations. This option is, however, neither necessary nor recommended in these cases.

For minimum internal temperature approach specifications, however, zones analysis is required at calculation time in order to accurately identify pinch points. Under these conditions, the weighted LMTD is used in equation (1).

Example

An example of a zones analysis of a countercurrent heat exchanger is given next, and shown in Figure 2.5.2-1.

Figure 2.5.2-1: Zones Analysis for Heat Exchangers



Consider a countercurrent heat exchanger with a hot side containing a superheated hydrocarbon-water vapor mixture which enters at temperature $T_{h(in)}$ (point 1). The hot fluid changes phase when it cools down to $T_{h(dewhc)}$, the dew point of the hydrocarbon. A zone boundary is created at this phase change. As the stream continues to cool, it changes phase yet again when it reaches the aqueous dew point $T_{h(dewaq)}$. Again, a zone boundary is created here. After further cooling, another phase change occurs at $T_{h(bub)}$, the bubble point of the stream, and continues to cool until it reaches $T_{h(out)}$ (point 2).

The cold side containing a subcooled liquid enters at temperature $T_{c(in)}$ (point 3), and is heated to the bubble point, $T_{c(bub)}$. A zone boundary is created at this point. The cool stream is further heated until it reaches the aqueous dew point, $T_{c(dewaq)}$. It is heated even further until it reaches the hydrocarbon dew point, $T_{c(dewhc)}$. Finally, it is heated until the final temperature of $T_{c(out)}$ (point 4) is reached. Based on phase change points alone, the maximum number of zones which may be created is seven as shown in Figure 2.5.2-1. Additionally, PRO/II will further subdivide these zones into smaller zones of equal DT. The calculation procedure is then as follows:

- The ends of the exchanger constitute the overall zone boundaries, and the total exchanger heat duty is calculated. If the overall U and A values are specified, the overall duty is estimated.
- The duty for each zone is calculated, and then the corrected LMTD values for each zone are obtained. Equation (2) is then used to determined the weighted average LMTD value for the exchanger.
- The heat transfer coefficients are calculated for each zone.
- The areas for each zone are determined using the zone values for U, Q, LTMD, and equation (1), and then are summed to give the heat transfer area for the entire exchanger.

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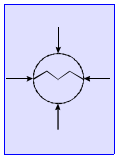
PRO/II Note: For more information on using a simple heat exchanger model in PRO/II, see Section 81, *Simple Heat Exchanger*, of the *PRO/II Keyword Input Manual*.

Reference

Bowman, R. A., Mueller, and Nagle, 1940, *Trans. ASME*, **62**, 283.

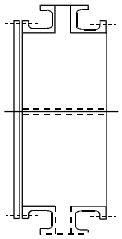
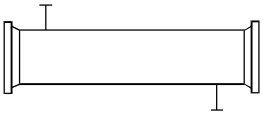
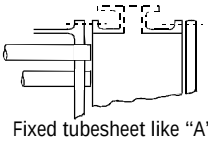
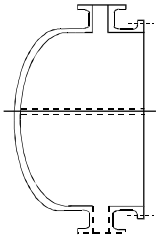
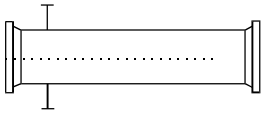
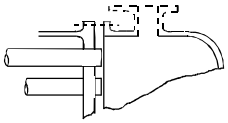
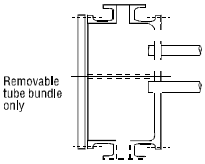
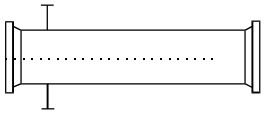
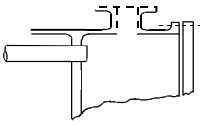
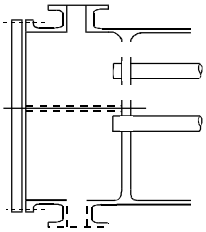
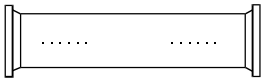
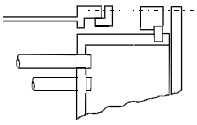
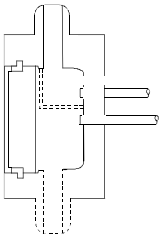
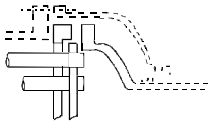
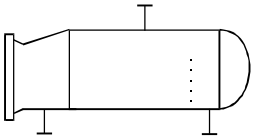
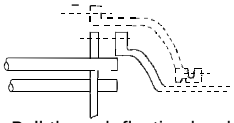
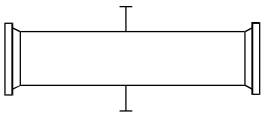
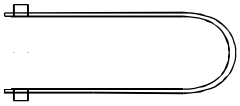
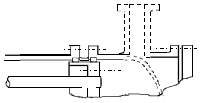


2.5.3 *Rigorous Heat Exchanger*

General Information

PRO/II contains a shell-and-tube heat exchanger module which will rigorously rate most standard heat exchangers defined by the Tubular Exchanger Manufacturers Association (TEMA). Shell and tubeside heat transfer coefficients, pressure drops, and fouling factors are calculated. The TEMA types available in PRO/II are given in Figure 2.5.3-1.

Figure 2.5.3-1: TEMA Heat Exchanger Types

	Front End Stationary Head Types		Shell Types		Rear End Head Types
A	 Channel and removable cover	E	 One pass shell	L	 Fixed tubesheet like “A” stationary head
B	 Bonnet (Integral cover)	F	 Two pass shell with longitudinal baffle	M	 Fixed tubesheet like “B” stationary head
C	 Channel integral with tubesheet and removable cover	G	 Split flow	N	 Fixed tubesheet like “N” stationary head
N	 Channel integral with tubesheet and removable cover	H	 Double split flow	P	 Outside packed floating head
D	 Special high pressure closure	J J1 J2	Divided flow	S	 Floating head with backing device
		K	 Kettle type reboiler	T	 Pull through floating head
		X	 Cross flow	U	 U-tube bundle
				W	 Externally sealed floating tubesheet

82

PRO/II Note: For more information on using a rigorous heat exchanger model in PRO/II, see Section 82, *Rigorous Heat Exchanger*, of the *PRO/II Keyword Input Manual*.

Heat Transfer Correlations

Shellside

The Bell-Delaware method is used to compute the heat transfer coefficient on the shellside. The method accounts for the effect of leakage streams in the shellside. The shellside heat transfer coefficient is given by:

$$h = h_{ideal} J_c J_l J_b J_s J_r \quad (1)$$

where:

h = average shellside heat transfer coefficient

h_{ideal} = shellside heat transfer coefficient for an ideal tube bank

J_c = correction factor for baffle cut and spacing

J_l = correction factor for baffle-leakage effects

J_b = correction factor for bundle bypass flow effects

J_s = correction factor for inlet and outlet baffle spacing

J_r = correction factor for adverse temperature-gradient build-up

The correction factor, J_c, is a function of the fraction of the total tubes in the crossflow; J_l is a function of the tube-to-baffle leakage area, and the shell-to-baffle leakage area; J_b is a function of the fraction of crossflow area available for bypass flow and the Reynolds number; J_s is a function of the baffle spacing; J_r is a function of the number of baffles. The Bell method is used to compute these correction factors.

The heat transfer coefficient for an ideal tube bank, h_{ideal}, is obtained from the following relationships:

$$N_{Nu(tur)} = \frac{0.037 N_G^{0.8} N_{Pr}}{1 + 2.443 N_{ReG}^{-0.1} \left(N_{Pr}^{2/3} - 1 \right)} \quad (2)$$

$$N_{Nu(lam)} = 0.664 N_{ReG}^{0.5} N_{Pr}^{1/3} \quad (3)$$

$$N_{Nu(bund)} = 0.3 + \left(N_{Nu(lam)}^2 + N_{Nu(tur)}^2 \right)^{0.5} \quad (4)$$

$$h_{ideal} = \frac{N_{Nu(bund)} k}{L} \quad (5)$$

where:

N_{ReG} = Reynolds number as defined by Gnielinski = $\frac{WL}{\varepsilon_F D_S l_b \mu_b}$

N_{Pr} = Prandlt number = $\frac{c\mu_b}{k}$

W = total mass flow rate in shellside

c = specific heat of fluid

ε_F = shell void fraction

D_s = shell inside diameter

l_b = baffle spacing

μ_b = fluid viscosity at bulk temperature

N_{Nu} = Nusselt number

k = thermal conductivity of shellside fluid

L = effective length of shell

subscripts *tur*, and *lam* refer to the turbulent and laminar flow regimes, and *bund* refers to the tube bundle.

Alternatively, the user may supply the shellside heat transfer coefficient directly.

Tubeside

For turbulent flow in circular tubes, the tubeside heat transfer coefficient is obtained from the Sieder-Tate equation:

$$N_{Nu} = \frac{hL}{k} = 0.023 N_{Re}^{0.8} N_{Pr}^{1/3} \left[\frac{\mu_w}{\mu_b}\right]^{-0.14} \quad (6)$$

where:

μ_w = fluid viscosity at the wall temperature

The above relationship holds for the following flow regimes:

$$matrix \begin{matrix} N_{Re} > 10000 \\ 0.7 < N_{Pr} < 700 \\ \frac{L}{D} > 60 \end{matrix}$$

where:

N_{Nu} = Nusselt number

N_{Re} = Reynolds number = $\frac{DW}{A_t \mu_b}$

N_{Pr} = Prandlt number

L = tube length

D = effective tube diameter

W = total mass flow rate in tubeside

A_t = cross sectional tube area

For laminar flow regimes, $N_{Re} < 2000$, a different relationship is used for the heat transfer coefficient, depending on the value of the Graetz number. The Graetz number, N_{Gz}, is defined as:

$$N_{Gz} = N_{\mathrm{Re}}\, N_{Pr} \left[\frac{D}{L}\right] \tag{7}$$

For $N_{Gz} < 100$, a relationship first developed by Hausen is used:

$$N_{Nu} = 3.66 + \frac{0.085 N_{Gz}}{1+0.047\, N_{Gz}^{2/3}} \left[\frac{\mu_b}{\mu_w}\right]^{0.14} \tag{8}$$

For $N_{Gz} > 100$, the Sieder-Tate relationship is used:

$$N_{Nu} = 1.86\, N_{Gz}^{1/3} \left[\frac{\mu_b}{\mu_2}\right]^{0.14} \tag{9}$$

For transition flow regimes where $2000 < N_{Re} < 10000$, the tubeside film coefficient is obtained by interpolation between those values calculated for the laminar and turbulent flow regimes:

$$h_{trans} = \frac{(h_{turb} - h_{lam})\,(N_{\mathrm{Re}} - 2000)}{8000} + h_{lam} \tag{10}$$

where:

h_{trans} = heat transfer film coefficient for the transition regime

h_{turb} = heat transfer film coefficient for the turbulent flow regime

h_{lam} = heat transfer film coefficient for the laminar flow regime

The user may also supply the film coefficients directly.

Pressure Drop Correlations

Shellside

The shellside pressure drop may be determined by one of two methods; the Bell-Delaware method, or the stream analysis method. The Bell-Delaware method, which is the default method used by PRO/II, uses the following procedure.

First, the pressure drop for an ideal window section is calculated using the following correlations:

For $N_{Re} < 100$,

$$\Delta P_{wi} = \frac{26\,\mu_b W}{g_c (S_m S_w)^{0.5}\,\rho} \left(\frac{N_{cw}}{p' - D_o} + \frac{l_b}{D_w^2}\right) + \frac{W^2}{g_c (S_m S_w)^{0.5}\,\rho} \tag{11}$$

For $N_{Re} > 100$,

$$\Delta P_{wi} = \frac{W^2 (2+0.6\, T_{cw})}{2 g_c S_m S_w \rho} \qquad (12)$$

The pressure drop for an ideal crossflow section is then calculated:

$$\Delta P_{bi} = \frac{4 f_k W^2 N_c}{2 \rho g_c S_m^2} \left[\frac{\mu_w}{\mu_b}\right]^{0.14} \qquad (13)$$

where:

f_k = the friction factor for the ideal tube bank calculated at the shellside Reynolds number

g_c = gravitational force conversion factor = 4.18 x 10^8 lbm-ft/lbf-hr

N_c = number of tubes in one crossflow section

N_{cw} = number of crossflow rows in each window

S_m = minimum cross sectional area between rows of tubes for flow normal to tube direction

S_w = cross sectional area of flow through window

D_o = outside exchanger diameter

D_w = equivalent diameter of a window

p' = tube pitch, center-to-center spacing of tubes in tube bundle

ρ = fluid density

The actual shellside pressure drop is obtained by accounting for the effects of bypasses and leakages, and is given by:

$$\Delta P_s = \left[(N_b - 1)\, \Delta P_{bi}\, R_b + N_b\, \Delta\, P_{wi}\right] R_l + 2\Delta\, P_{bi} R_B R_s \left(1 + \frac{N_{cw}}{N_c}\right) \qquad (14)$$

where:

ΔP_s = actual shellside pressure drop

N_b = number of segmental baffles

R_b = bundle bypass flow correction factor

R_l = baffle leakage effects correction factor

R_s = correction factor for unequal baffle spacing effects

The stream analysis method, proposed in 1984 by Willis and Johnson, is an iterative, analytical method. At each iteration the crossflow resistance, R_c, the window flow resistance, R_w, the tube to baffle resistance, $R_{t\text{-}b}$, the shell to baffle resistance, $R_{s\text{-}b}$, the leakage resistance, R_l, the flowrate through the windowed area, W_w, the crossflow pressure drop, ΔP_c, the window pressure drop, ΔP_w, and the crossflow fraction, F_c are calculated as follows:

$$R_c = function\ (D_c,\ tube\ bank\ layout,\ \rho, S_c) \tag{15}$$

$$R_w = \frac{1.9\exp\left(\frac{0.6856 S_w}{S_m}\right)}{2\rho S_w^2} \tag{16}$$

$$R_{t-b} = func(tube\text{–}to\text{–}baffle clearance,\ tube\text{–}to\text{–}baffle\ leakage\ area,\ \rho,\ \mu) \tag{17}$$

$$R_{s-b} = func(shell\text{–}to\text{–}baffle clearance,\ shell\text{–}to\text{–}baffle\ leakage\ area,\ \rho,\ \mu) \tag{18}$$

$$R_l = func\left(R_{t-b}, R_{s-b}\right) \tag{19}$$

$$W_w = \frac{W}{1 + \left[\frac{R_w + R_c}{R_l}\right]^{0.5}} \tag{20}$$

$$\Delta P_c = R_c W_w^2 \tag{21}$$

$$\Delta P_w = R_w W_w^2 \tag{22}$$

$$F_c = \frac{(\Delta P_c / R_c)^{0.5}}{W} \tag{23}$$

where:

S_c = crossflow area

D_c = crossflow equivalent diameter

Iterations are stopped once the value of F_c meets the following criterion:

$$\left|\frac{(F_{c,iter} - F_{c,iter-1})}{F_{c,iter}}\right| < 0.01 \tag{24}$$

The shellside end space pressure drops at the inlet and outlet of the exchanger, $\Delta P_{s,in}$, and $\Delta P_{s,out}$, and the actual shellside pressure drop, ΔP_{ss}, are then calculated using the equations:

$$\Delta P_{s,in} = \overline{R_{s,in} W_{in}^2} \quad (25)$$

$$R_{s,in} = function(R_c, l_b, S_m, S_w, \rho) \quad (26)$$

$$\Delta P_{s,out} = \overline{R_{s,out} W_{out}^2} \quad (27)$$

$$R_{s,in} = function(R_c, l_b, S_m, S_2, \rho) \quad (28)$$

$$\Delta P_{ss} = \frac{\Delta P_{s,in} + (N_b - 1)(\Delta P_c + \Delta P_w) + \Delta P_{s,out}}{g_c} \quad (29)$$

where:

$\Delta P_{s,in}$ = mean shellside end space pressure drop at exchanger inlet

$\Delta P_{s,out}$ = mean shellside end space pressure drop at exchanger outlet

$R_{s,in}$ = end space resistance at exchanger inlet

$\overline{R_{s,out}}$ = end space resistance at exchanger outlet

$\overline{\quad}$ = denotes an average

Tubeside

The tubeside pressure drop, ΔP_{ts}, is calculated as the sum of the pressure drops in the tubes plus the pressure drops in the return bends:

$$\Delta P_t = \frac{F G_t^2 L n}{4.35 x 10^9 D_i S_p \mu_c} \quad (30)$$

$$\Delta P_r = \frac{2 n G_t^2}{(2.741 x 10^6 S_p)^2} \quad (31)$$

$$\Delta P_{ts} = \Delta P_t + \Delta P_r \quad (32)$$

where:

ΔP_t = pressure drop in tubes

ΔP_r = pressure drop in return tubes

ΔP_{ts} = total pressure drop in the tubeside

μ_c = fluid viscosity factor

F = friction factor

G_t = mass flux

L = tube length

n = number of tube passes

D_i = tube inner diameter

S_p = specific gravity of fluid

The friction factor, F, and viscosity factor, μ_c are computed using different correlations for each flow regime:

For turbulent flows, $N_{Re} > 2800$,

$$\mu_c = \left[\frac{\mu_b}{\mu_2}\right]^{0.14} \quad (33)$$

$$\log_{10} F = -0.2643 \log_{10} N_{Re} - 2.5103 \quad (34)$$

For laminar flows, $N_{Re} < 2100$,

$$\mu_c = \left[\frac{\mu_b}{\mu_2}\right]^{0.25} \quad (35)$$

$$\log_{10} F = -0.9952 \log_{10} N_{Re} - 0.31537 \quad (36)$$

For transition flow regimes, $2100 < N_{Re} < 2800$, F and μ_c are obtained by interpolation between the laminar and turbulent values:

$$\mu_c = \frac{(\mu_{c,tur} - \mu_{c,lam)}\,(N_{Re} - 2100)}{700} + \mu_{c,lam} \quad (37)$$

$$F = \frac{(F_{tur} - F_{lam})\,(N_{Re} - 2100)}{700} + F_{lam} \quad (38)$$

Fouling Factors

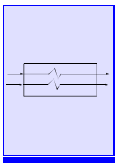
In most exchanger applications, the resistance to heat transfer increases with use as a result of scaling caused by crystallization or deposition of fine material. These factors may or may not increase the pressure drop in the exchanger. For both the tubeside and shellside, the user may input separate factors to account for thermal and pressure drop resistances due to exchanger fouling.

Thermal fouling resistances cannot be calculated analytically. Tables for thermal heat transfer coefficients (the inverse of thermal resistances) for a number of common industrial applications may be obtained from standard references on heat exchangers such as Perry's handbook, or the book by Kern.

PRO/II also allows the user to account for the effect of fouling on pressure drop by inputting a thickness of fouling layer.

References

1. Perry, R. H., and Chilton, C. H., 1984, Chemical Engineers Handbook, 6th Ed.
2. Kern, 1950, Process Heat Transfer, McGraw-Hill, N.Y.
3. Gnielinski, V., 1979, *Int. Chem. Eng.*, **19**(3), 380-400.
4. Willis, M. J. N., and Johnston, D., 1984, A New and Accurate Hand Calculation Method for Shellside Pressure Drop and Flow Distribution, paper presented at the 22nd Heat Transfer Conference, Niagara Falls, N.Y.



2.5.4 LNG Heat Exchanger

General Information

PRO/II contains a model for a LNG (Liquified Natural Gas) heat exchanger. This type of exchanger is also called a ‘‘Cold Box’’ and simulates the exchange of heat between any number of hot and cold streams. An advantage of this type of exchanger is that it can produce close temperature approaches which is important when cooling close boiling point components. Typically, LNG exchangers are used for cryogenic cooling in the natural gas and air separation industries.

Calculation Methods

The LNG exchanger is divided into hot or cold ‘‘cells’’ representing the individual cross-flow elements. Cold cells represent areas where streams are cooled, while hot cells represent areas where streams are heated. The following assumptions apply to the LNG heat exchanger:

- Each LNG exchanger must have at least one hot and one cold cell.
- The exchanger configuration is ignored.
- At least one cell does not have a product specification and all unspecified cells leave at the same temperature.

Equation (1) applies to every cell in the LNG exchanger:

$$\delta q_{cell} = H_{out} - H_{in} = mc_p\,(T_{out} - T_{in}) \qquad (1)$$

where:

δq_{cell} = heat transferred in exchanger cell
H_{out} = enthalpy of stream leaving the cell
H_{in} = enthalpy of stream entering the cell

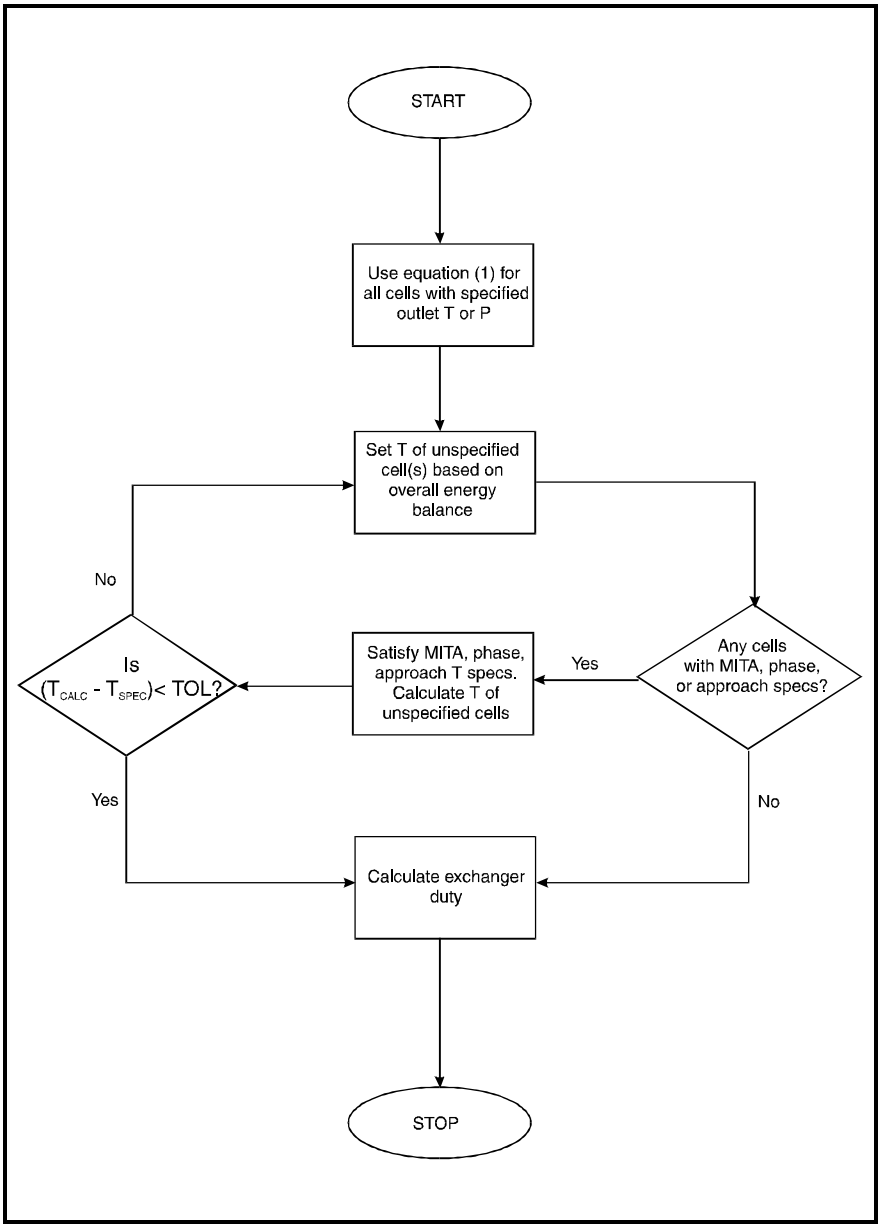
The following specifications may be set for a LNG cell:

- Outlet temperature, T_{out}.
- Cell duty, δq_{cell}.
- Phase of outlet stream.
- Hot-cold stream temeprature approaches.
- Minimum internal temeprature approach (MITA).

Note: The last three specifications listed above (outlet phase, temperature approach, and MITA) can only be accomplished using a feedback controller unit.

Figure 2.5.4-2 shows the algorithm used to solve an LNG exchanger:

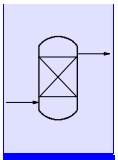
Figure 2.5.4-2: LNG Exchanger Solution Algorithm


START
Use equation (1) for all cells with specified outlet T or P
Set T of unspecified cell(s) based on overall energy balance
Any cells with MITA, phase, or approach specs?
Yes
Satisfy MITA, phase, approach T specs. Calculate T of unspecified cells
Is (T CALC - T SPEC)< TOL?
No
Yes
No
Calculate exchanger duty
STOP

Zones Analysis

When phase changes occur within the LNG heat exchanger, PRO/II can perform a Zones Analysis to locate and report any internal temperature pinches or crossovers. For the LNG exchanger, the UA and LMTD for the exchanger are calculated using the composite hot and cold streams.

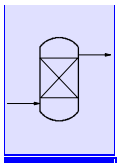
Note: See Section 2.5.2, *Zones Analysis*, for more details.



2.6 Reactors

PRO/II offers the following chemical reactors:

- Conversion Reactor, which can operate at a desired conversion level
- Equilibrium Reactor
- Gibbs Free Energy Minimization Reactor
- Ideal Mixed Flow Reactor (Continuous Stirred Tank Reactor or CSTR)
- Ideal Tubular Reactor (Plug Flow Reactor or PFR)



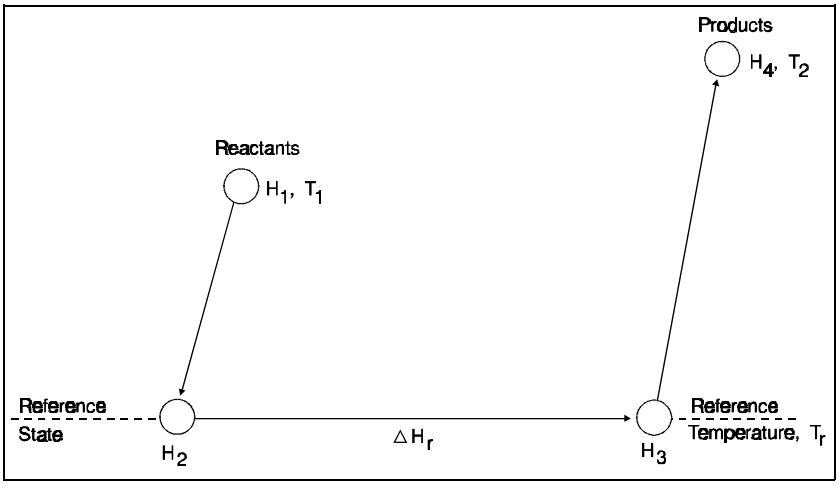
2.6.1 Reactor Heat Balances

The heats of reaction for all reactors are determined in one of two ways:

- The user may supply the heat of reaction for each stoichiometric reaction in the Reaction Data section. This heat must be given at a reference temperature and phase, either vapor or liquid. PRO/II will not accept a mixed-phase reference basis.
- If the heat of reaction is not supplied, the heat of reaction will be calculated from heat of formation data. PRO/II has heat of formation data available for all library components at 25°C, vapor phase. PRO/II will estimate the heats of formation for all PETRO components. The heat of formation data may be overridden for all LIBID and PETRO components. If NONLIB components are used, the heat of formation data should be provided by the user at the same reference conditions as all other components.

Once the heat of reaction data are supplied, PRO/II can calculate the total enthalpy change along the reaction path as shown in Figure 2.6.1-1

Figure 2.6.1-1 Reaction Path for Known Outlet Temperature and Pressure



a) The reactants are brought to the reference temperature and phase. The enthalpy difference, H_2-H_1 is calculated by the prevailing enthalpy calculation methods for that reactor.

b) The total heat of reaction, ΔH_r, is then calculated by summing all the individual heats of reaction occurring in the reactor.

c) The reactor effluents are brought to the outlet thermal conditions resulting in H_4.

$$Duty = (H_2 - H_1) + \Delta H_r + (H_4 - H_3) \quad (1)$$

The total reactor duty is the sum of the individual path duties. This process is completely independent of enthalpy datum, hence users can supply enthalpy values at any arbitrary datum with good results.

For vapor phase reactions, the reference pressure is taken as 1 atm. Should the reference phase condition (checked by the flash operation) be found to be liquid for either the reactants or products, the pressure is lowered further until only vapor is present. Similarly, for the liquid phase reactions, the reference pressure of reactants or products is increased until only liquid is present.

When the ADIABATIC option is active, duty may be supplied on the OPERATION statement. (Unlike the FLASH unit operation, the reactor also has reference state enthalpies H_2 and H_3 and heat of reaction ΔH_r which can be changed, and which will change the outlet enthalpy. An adiabatic reactor will actually be a fixed-duty reactor.) The outlet temperature is determined by trial and error to satisfy the duty.

The reactor duty can be calculated from equation (1).

The heat balance will be printed in the reactor summary if the PRINT PATH statement is input.

Heat of Reaction

The heat of reaction may be furnished by the user as a function of the moles of base component reacted. Alternatively, the heat of reaction will be computed by PRO/II if not supplied, through the following relationship:

$$\Delta H_r = \sum \Delta H_{f,\,products} - \sum \Delta H_{f,\,reactants} \quad (2)$$

where:

ΔH_f = heat of formation of each component at 25 °C

Heat of formation data are available in the component databank for library components and can be estimated for petroleum components using internal correlations. For NONLIBRARY components this data must be furnished.

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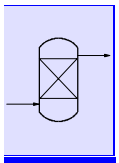
PRO/II Note: If it is desired not to calculate the heat of reaction, the NOHBAL option should be selected on the RXCALCULATION statement.



2.6.2 Conversion Reactor

The CONREACTOR unit operation is a simple conversion reactor. No kinetic information is needed nor are any reactor sizing calculations performed. The desired conversion of the base component is specified and changes in the other components will be determined by the corresponding stoichiometric ratios. Conversions may be specified as a function of temperature, as follows:

$$Fractional\ Conversion = C_0 + C_1 T + C_2 T^2 \qquad (1)$$

where:

T is in problem temperature units
C_0, C_1, C_2 are constants

The fractional conversion could be based either on the amount of base component in the feed to the reactor (feed-based conversion) or on the amount of base component available for a particular reaction (reaction-based conversion). The former concept is suitable for specifying conversions in a system of parallel reactions, whereas the latter definition is more appropriate for sequential or series reactions. PRO/II will select feed-based conversion as the default conversion basis for single, parallel and series-parallel reactions. Reaction-based conversion is the default conversion basis for series reactions. If specified explicitly, the method (FEED or REACTION) selected with the CBASIS keyword will be used. In any case, the fractional conversion value input with the CONVERSION statement will be understood to have as its basis the default or input CBASIS, whichever is applicable.

The reactor may be operated isothermally at a given temperature, adiabatically (with or without heat duty specified), or at the feed temperature. For adiabatic reactors, heat of reaction data must be given or should be calculable from the heat of formation data available in the component library databank. Temperature constraints can be specified. For isothermal reactors, the heat of reaction data is optional. If supplied, the required heat duty will be calculated.

An unlimited number of simultaneous reactions may be considered.

The conversion reactor can also be used to model shift and methanation reactors. In this case, fractional conversions can be specified for the shift and methanation reactions.

Shift Reactor Model

The purpose of the shift reactor model is to simulate the shift conversion of carbon monoxide into carbon dioxide and hydrogen with steam:

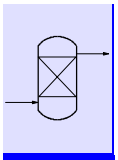
$$CO + H_2O = CO_2 + H_2 \quad (2)$$

Methanation Reactor Model

Methanators are used to convert the excess CO from the shift reaction into methane. The reactor model is similar to the shift reactor but both the methanation and shift reactions take place simultaneously.

$$CO + 3H_2 = CH_4 + H_2O \quad (3)$$

$$CO + H_2O = CO_2 + H_2$$



2.6.3 Equilibrium Reactor

The EQUREACTOR unit operation is a simple equilibrium reactor. No kinetic information is needed nor are any reactor sizing calculations performed. Equilibrium compositions are calculated based on equilibrium constant data. Approach data, if specified, are used to compute approach to equilibrium.

The reactor may be operated isothermally at a given temperature, adiabatically (with or without heat duty specified), or at the feed temperature. For adiabatic reactors, heat of reaction data must be given or should be calculable from the heat of formation data available in the component library databank. Temperature constraints can be specified. For isothermal reactors, the heat of reaction data is optional. If supplied, the required heat duty will be calculated.

A single reaction is considered for the stoichiometric and simultaneous equilibria of two reactions are computed for the methanator model.

For chemical equilibrium calculations in PRO/II, ideal behavior is assumed for reaction in either the liquid or vapor phase.

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PRO/II Note: Select the required phase using the PHASE entry of the OPERATION statement.

For a reaction,

$$a\,A + b\,B = c\,C + d\,D \qquad (1)$$

The equilibrium constant is:

for vapor phase:

$$K_{eq} = \frac{p_C^c\, p_D^d}{p_A^a\, p_B^b} \qquad (2)$$

for liquid phase:

$$K_{eq} = \frac{x_C^c\, x_D^d}{x_A^a\, x_B^b} \qquad (3)$$

where:

p = the partial pressure of component

x = the mole fraction of component in the liquid

Note: K_{eq} is dimensionless for liquid phase reactions and has the dimension of (pressure unit)$^{\alpha}$ with α = c + d - a - b for vapor phase reactions.

The temperature dependency of the equilibrium constant is expressed as:

$$\ln(K_{eq}) = A + \frac{B}{T} + C*\ln(T) + D*T + E*T^2 + F*T^3 + G*T^4 + H*T^5 \quad (4)$$

where:

K_{eq} = reaction equilibrium constant
A-H = Arrhenius coefficients
T = absolute temperature

When no approach data are given, all reactions go to equilibrium by default. The approach to equilibrium can be given either on a fractional conversion basis or by a temperature approach. The conversion itself can be specified as a function of temperature.

When the temperature approach is given, K_{eq} is computed at T, where:

$T = T_{reaction - \Delta T}$ (endothermic reactions)
$T = T_{reaction + \Delta T}$ (exothermic reactions)

Based on the value of K_{eq}, conversion of base component and product compositions can be calculated.

If the approach to equilibrium is specified on a fractional conversion basis, the conversion of the base component B, is given by:

$$C_B = \left(B_F - B_R\right) = \Delta\left(B_F - B_E\right) \quad (5)$$

where:

B_R = moles of component B in the product
B_F = moles of component B in the feed
B_E = moles of component B at equilibrium
Δ = specified approach to equilibrium
= $C_0 + C_1T + C_2T^2$

The coefficients C_0, C_1, and C_2 may appear in any combination, and missing values default to zero. For a fixed approach, C_1 and C_2 are zero. When no approach data are given, reactions attain equilibrium, and C_0=1.0, C_1=0.0, and C_2=0.0.

The equilibrium reactor can also be used with specialized reactor models for shift and methanation reactions.

Shift Reactor Model

The purpose of the shift reactor model is to simulate the shift conversion of carbon monoxide into carbon dioxide and hydrogen with steam:

$$CO + H_2O = CO_2 + H_2 \quad (6)$$

Just as in the Stoichiometric Reactor, the desired conversion is determined from an equilibrium model for the shift reaction. PRO/II has incorporated the National Bureau of Standards data for equilibrium constants. This can be represented by:

$$\ln(K_{eq}) = A + \frac{B}{T} \quad (7)$$

where:

A and B are functions of temperature

T = absolute temperature, R

and

$$K_{eq} = \frac{p_{CO_2} p_{H_2}}{p_{CO} p_{H_2O}} \quad (8)$$

where:

p = partial pressure in any units

If desired, users may override the NBS data and supply their own constants A and B in the above equation.

The approach to equilibrium can also be indicated either on a fractional conversion basis or by a temperature approach.

Methanation Reactor Model

Methanators are used to convert the excess CO from the shift reaction into methane. The reactor model is similar to the shift reactor but both the methanation and shift reactions take place simultaneously. It can also be used to model the reverse reaction viz., steam reforming of methane to yield hydrogen. These are:

$$CO + 3H_2 = CH_4 + H_2O \quad (9)$$

$$CO + H_2O = CO_2 + H_2$$

Just as for the shift reaction, the National Bureau of Standards data are available for methanation reaction. The methanation equilibrium is given by:

$$K_{eq} = \frac{p_{CH_4} p_{H_2O}}{p_{CO} p_{H_2}^3} \quad (10)$$

where:

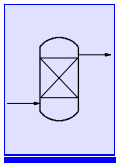
p = partial pressure in psia

Calculation Procedure for Equilibrium

For adiabatic, equilibrium models, the calculation procedure is as follows:

1. Assume an outlet temperature.
2. Determine the equilibrium constant at the assumed temperature plus the approach to equilibrium.
3. Calculate the product compositions from K_{eq} for the reaction.
4. Calculate the conversion and adjust by the fractional approach to equilibrium.
5. Calculate the enthalpy of products and perform an adiabatic flash to determine the outlet temperature.
6. If the calculated and assumed temperatures do not agree, repeat the calculations with the new temperature.

Only one approach to equilibrium, i.e., either a temperature approach or a fractional conversion approach, is allowed.



2.6.4 Gibbs Reactor

General Information

The Gibbs Reactor in PRO/II computes the distribution of products and reactants that is expected to be at phase equilibrium and/or chemical equilibrium. Components declared as VL or VLS phase type can be in both chemical and phase equilibrium. Components declared as LS or S type are treated as pure solids and can only be in chemical, but not phase, equilibrium. The reactor can be at either isothermal or adiabatic conditions. Reaction and product specifications can be applied to impose constraints on chemical equilibrium. Available constraints include fixed product rates, fixed percentage of feed amount reacted, global temperature approach, and reaction extent or temperature approach for each individual reaction. The mathematical model does not require the knowledge of reaction stoichiometry from the user except when the reaction extent or a temperature approach is to be specified for the individual reaction.

Mathematics of Free Energy Minimization

Objective Function of Gibbs Free Energy Minimization

The objective function which is to be minimized is composed of two parts. The first is the total Gibbs free energy of the mixture in all phases.

$$\frac{G}{RT} = \sum_{j=1}^{NS} \frac{G_j^{OC}}{RT} n_j^c + \sum_{p=1}^{NP} \sum_{j=1}^{NC} \frac{G_{jp}}{RT} n_{jp} \qquad (1)$$

where:

NS =	number of solid components
NP =	number of fluid phases
NC =	number of fluid components
G_j^{0C} =	Gibbs free energy of solid component at standard state
G_{jp} =	Gibbs free energy of fluid component at reactor temperature and pressure
T =	reactor temperature
n_j^C =	number of moles of solid component
n_{jp} =	number of moles of fluid component

In the design equation (1) the Gibbs free energy is represented by a quadratic function.

$$G(N) = G(n) + \Delta G^T(n)\,(N-n) + \frac{1}{2}(N-n)^T\ \Delta^2 G\,(N-n) \qquad (2)$$

When a temperature approach is applied for all reactions (global approach) or for individual reactions (individual approach), the standard state free energies of formation are modified in a way that the relation between the reaction equilibrium constant and change of Gibbs free energy of formation is satisfied (see equation (3)). The standard state Gibbs free energy is defined as at reactor temperature, 1 atm, and ideal gas state for all fluid components, and at reactor temperature, 1 atm, and solid state for all solid components

$$K_j = \exp(-\Delta G_j / RT') \qquad j = 1,..., NR \qquad (3)$$

where:

NR = number of reactions

ΔG_j = change of Gibbs free energy of formation at modified temperature T

T' = T + ΔT

ΔT = temperature approach

The second part of the objective function is the conservation of element groups and mass balance equations created from the constraints on chemical equilibrium. For each element group, the output flowrate has to be equal to the feed flowrate, i.e.:

$$b_k = \sum_{j=1}^{NS} m_{jk} n_j^c + \sum_{p=1}^{NP} \sum_{j=1}^{NC} m_{jk}\, n_{mp} \qquad k=1,..., NE \qquad (4)$$

where:

b_k = feed quantity of element group k

NE = number of element groups

m_{jk} = number of element group k contained in component j

If the product rate of a component is fixed, either by the constraint of fixed product rate or by the fixed percentage of feed amount reacted, the additional mass balance constraint can be written as:

$$d_j = n_j^c \qquad j=1,...,NSFIX \qquad (5a)$$

or

$$d_j = \sum_{j=1}^{NP} n_{jp} \qquad j=1,...,NCFIX \qquad (5b)$$

where:

d_j = specified or derived fixed product rate

$NSFIX$ = number of solid components with fixed product rate

$NCFIX$ = number of fluid components with fixed product rate

If a reaction has a specified reaction extent, the additional mass balance constraint is:

$$\xi r = \sum_{j=1}^{NS} a_{rj}\,(n_j^c - n_j^{oc}) - \sum_{j=1}^{NR-NS} a_{rj}\left[\sum_{p=i}^{NP} n_{jp} - n_j^0\right] \qquad r=1,\ldots, NR \tag{6}$$

where:

ξ_r = fixed reaction extent

a_{rj} = matrix element derived from the inverse of stoichiometric coefficient matrix

From equations (1), (4), (5), and (6), the overall objective function for the minimization of Gibbs free energy can be expressed as equation (7):

$$F(n) = G(n) + RT\left[\sum_{k=1}^{NE}\pi_k\left\{b_k - \sum_{j=1}^{NS} m_{jk}\,n_j^c - \sum_{p=1}^{NP}\sum_{j=1}^{NC} m_{jk}\,n_{jp}\right\}\right.$$
$$+\sum_{r=1}^{NR}\pi_r\left[\xi_r - \sum_{j=1}^{NS} a_{rj}\,(n_j^c - n_j^{oc}) - \sum_{j=1}^{NR-NS} a_{rj}\left(\sum_{p=1}^{NP} n_{jp} - n_j^o\right)\right]$$
$$\left.+\left\{\sum_{j=1}^{NSFIX}\pi_j\,(d_j - n_j^c) + \sum_{j=1}^{NCFIX}\pi_j\left(d_j - \sum_{p=1}^{NP} n_{jp}\right)\right\}\right] \tag{7}$$

In equation (7) above, π's are the Lagrange multipliers for the conservation of elemental groups and various mass balance equations.

Solution of Gibbs Free Energy Minimization

The necessary conditions for a minimum value of F(n) are:

$$\frac{\partial F(n)}{\partial n_j^c} = 0 \qquad j=1,\ldots, NS \tag{8}$$

$$\frac{\partial F(n)}{\partial n_{jp}^c} = 0 \qquad j=1,\ldots, NC;\ \ p=1,\ldots,NP$$

$$\frac{\partial F(n)}{\partial \pi_k} = 0 \qquad k=1,\ldots, NE$$

$$\frac{\partial F(n)}{\partial \pi_r} = 0 \qquad r=1,\ldots, NR$$

$$\frac{\partial F(n)}{\partial \pi_j} = 0 \qquad j=1,\ldots, NSFIX$$

$$\frac{\partial F(n)}{\partial \pi_j} = 0 \qquad j=1,\ldots, NCFIX$$

Note that since these are the necessary, but not the sufficient, conditions for Gibbs free energy minimization, a local minimum Gibbs free energy can be obtained. Multiple solutions may be found when multiple fluid phases coexist in the mixture. Providing different initial estimates for different runs can be used as a way to check whether solution corresponding to a local minimum Gibbs free energy has been reached.

The new solution point in each calculation iteration is determined by:

$$N' = n + \lambda(N - n) \qquad (9)$$

where:

n = the solution point from previous iteration

N = the new solution point from equation (8)

λ = step size parameter

The parameter λ is adjusted to ensure the new solution point, N′ will further minimize Gibbs free energy. A Fibonacci search procedure is applied when λ is close to zero. When a Fibonacci search is performed, the thermophysical properties of the reactor mixture can be either based on the same properties from the final result of the previous iteration or updated at each searching step of a new λ.

The convergence criterion is based on the relative or absolute change of Gibbs free energy and the relative change of component product rate between two consecutive iterations:

$$\left| G^{(r)} - G^{(r-1)} \right| \le \delta \quad \text{if} \left| G^{(r-1)} \right| \le \delta^2 \qquad (10)$$

or

$$\left| \frac{G^{(r)} - G^{(r-1)}}{G^{(r-1)}} \right| \le \delta \quad \text{if} \left| G^{(r-1)} \right| \le \delta^2$$

and

$$\left| \frac{N_j^{c(r)} - n_j^{c(r-1)}}{n_j^{c(r-1)}} \right| \le \delta \quad \text{if} \left| n_j^{c(r)} - n_j^{c(r-1)} \right| > 0.01\,\delta$$

and

$$\left| \frac{n_{jp}^{(r)} - n_{jp}^{(r-1)}}{n_{jp}^{(r-1)}} \right| \le \delta \quad \text{if} \left| n_{jp}^{(r)} - n_{jp}^{(r-1)} \right| > 0.01\,\delta$$

The variable δ is the convergence tolerance, which is defaulted to 1.0E-4 and can be specified by the user. The precision limit for a component product flowrate in any phase is 0.01δ. For any change in the product rate less than this value, the solution will be considered to be converged.

Phase Split

When a fluid phase condition of either vapor, liquid, vapor-liquid, liquid-liquid, or vapor-liquid-liquid, is specified for the reactor, the Gibbs free energy of fluid components is calculated based on the specified fluid phases. On the other hand, if the fluid phase is unknown or not specified for the reactor, phase split trials can be performed to evaluate the number of fluid phases in the reactor. The starting iteration number and the frequency of phase split trial can be adjusted by the user. In each phase split trial, a new fluid phase is added to the current fluid phases. If the Gibbs free energy is reduced as a result of adding this new phase, the new fluid phase is accepted.

The reactor modeling generally follows the algorithm described in the papers of Gautam *et al.* (1979) and White *et al.* (1981). Additional information can be found in the book by Smith (1991).

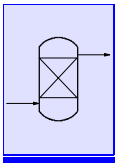
References

1. Gautam, R., and Seider, W.D., 1979, Computation of Phase and Chemical Equilibrium, Part I, *AIChE J.*, 25, 991-999.

2. Gautam, R., and Seider, W.D., 1979, Computation of Phase and Chemical Equilibrium, Part II, *AIChE J.*, 25, 999-1006.

3. White, C.W., and Seider, W.D., 1981, Computation of Phase and Chemical Equilibrium, Part IV, *AIChE J.*, 27, 466-471.

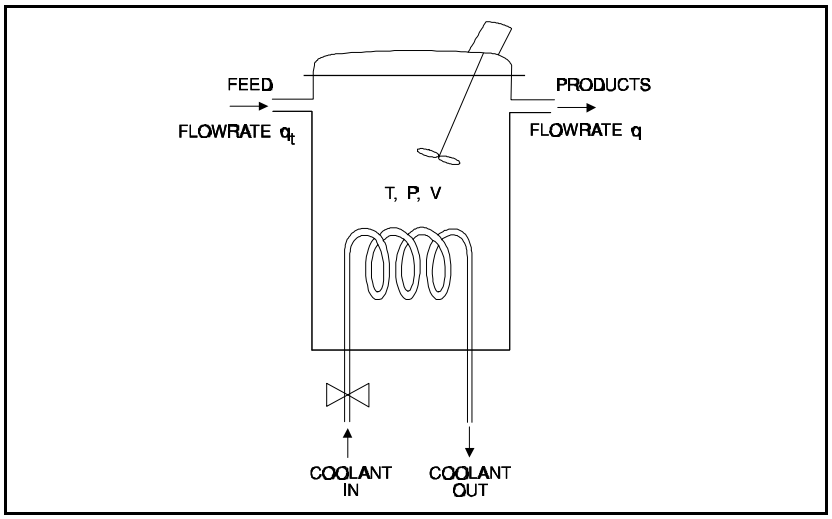
4. Smith, W.R., and Missen, R.W., 1991, Chemical Reaction Equilibrium Analysis: Theory and Algorithm, Krieger Publication Company, Malabar, Florida.



2.6.5 Continuous Stirred Tank Reactor (CSTR)

The Continuous flow Stirred Tank Reactor (CSTR) is a commonly used model for many industrial reactors. The CSTR assumes that the feed is instantaneously mixed as it enters the reactor vessel. Heating and cooling duty may be supplied at user's discretion. A schematic of a CSTR is given in Figure 2.6.5-1

Figure 2.6.5-1: Continuous Stirred Tank Reactor



Design Principles

The steady-state conservation equations for an ideal CSTR with M independent chemical reactions and N components (species) can be derived as:

Mass balance:

$$F_j = F_{jf} + \sum_{i=1}^{M} \alpha_{ij} \Re_i (T,P,C_1,C_2,.....,C_N)\, V \qquad (1)$$

Energy balance:

$$\left(\sum_{j=1}^{N} F_{jf}\right) H(T_f) - \left(\sum_{j=1}^{N} F_{jf}\right) H(T) + \sum_{i=1}^{M} (-\Delta H_i)\, \Re_i V - Q^* = 0 \qquad (2)$$

where:

C_j = exit concentration of j^{th} component

F_j = mole rate of component j in product

F_{jf} = mole rate of component j in feed

P = reactor pressure

α_{ij} = stoichiometric coefficient of jth species for ith reaction

V = volume of the reacting phase

$\Re_i$ = rate of ith reaction

$H(T)$ = molar enthalpy of product

$H(T_f)$ = molar enthalpy of feed

T_f = feed temperature

T = reactor temperature

ΔH_i = molar heat of reaction for the ith reaction

Q^* = heat removed from the reactor

In PRO/II, only power law models for kinetics are provided. However, any kinetic model can be introduced through the user-added subroutines feature in PRO/II. For further details, refer to Chapter 7 of the *PRO/II User-added Subroutines User's Manual.* The resulting general expression for the rate of the ith reaction is:

$$\Re_i = A_i \exp\left\{-\frac{E_i}{RT}\right\} T^{\alpha} \prod_{j=1}^{N} C_j^{\gamma_j} \qquad (3)$$

where:

A_i = Arrhenius frequency factor

E_i = activation energy, energy/mol

R = gas constant

T = temperature

α = temperature exponent

C_j = concentration of jth species

N = total number of reacting components

γ_j = exponents of concentration

$\Re_i$ = reaction rate for reaction i.

For multiple, simultaneous reactions, the overall reaction rate for each reacting component is:

$$\Re_j^* = \sum_{i=1}^{M} \alpha_{ij} A_i \exp\left\{-\frac{E_i}{RT}\right\} T^{\alpha} \prod_{j=1}^{N} C_j^{\gamma_j} \qquad (4)$$

where:

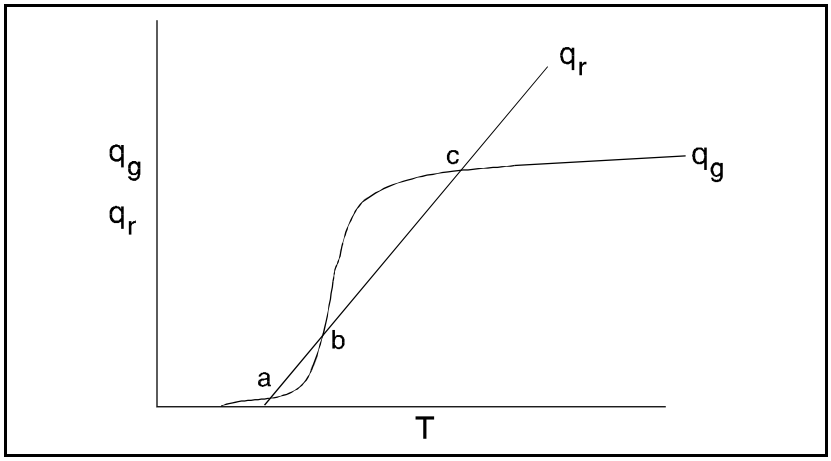
$\Re_j^*$ = net rate of production of species j.

Solution of a CSTR involves the simultaneous solution of equation (1) and equation (2).

Multiple Steady States

Adiabatic, exothermic reactions in CSTRs may have two valid steady state solutions, as illustrated in Figure 2.6.5-2.

Figure 2.6.5-2: Thermal Behavior of CSTR



The q_r line represents heat removal and is linear with increase in temperature. The q_g curve represents heat generation. At low temperatures, the curve increases exponentially with temperature due to increased reaction rate. As the reactants are exhausted, the extent of reaction levels off. Thus, there are three places where the two curves intersect. The top and bottom intersections represent stable solutions. The middle one represents the ‘‘ignition’’ temperature. Reactors above that temperature tend to stabilize at the high reaction rate and reactors below that temperature tend to stabilize at the low reaction rate.

In the PRO/II CSTR unit operation, either solution is possible and there is no built-in logic to ascertain that the correct solution is found. The final solution can be influenced by the addition of an initial estimate on the OPERATIONS statement. Generally, the CSTR will find the high temperature solution if the initial estimate is above the ignition temperature and the low temperature solution for initial estimates below the ignition temperature.

For some exothermic reactions and for all endothermic reactions there may be only one intersection between the heat generation and heat removal curves, indicating only one steady state. PRO/II readily finds this solution.

Boiling Pot Model

When the CSTR is operated as a boiling pot reactor, the reactions take place in the liquid phase, and the vapor product, in equilibrium with the reacting liquid, is drawn off.

From a degree of freedom analysis for the boiling pot reactor,

Variables: T, P, Q, F, X_j, Y_j, V Total = 2N + 5

Equations: Material Balance, equation (1)

$$K_j = y_j / x_j$$

$$\sum x_j = \sum y_j = 1$$ Total = 2N + 3

Reaction rate, equation (3)
Energy balance, equation (2)

The degrees of freedom or the number of variables to be fixed is 2. The rest of the variables or unknowns are then calculated by solving the model equations. Since the pressure P is fixed by the CSTR input, the user can choose to fix one of the other variables T, Q, or V. This leads us to the discussion on the possible operational modes of the CSTR.

CSTR Operation Modes

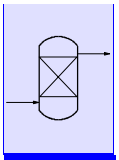
The possible operational modes for the CSTR are:

- adiabatic (fixed or zero heat duty).
- isothermal (fixed temperature)

In addition, for the boiling pot model, there is another optional mode of operation,

- isometric (fixed volume of reacting liquid phase).

The reactor volume is required for the vapor and liquid models. The pressure specification is fixed for all three models when input explicitly as the operating pressure or pressure drop, or when calculated as the pressure of the combined feed to the reactor.

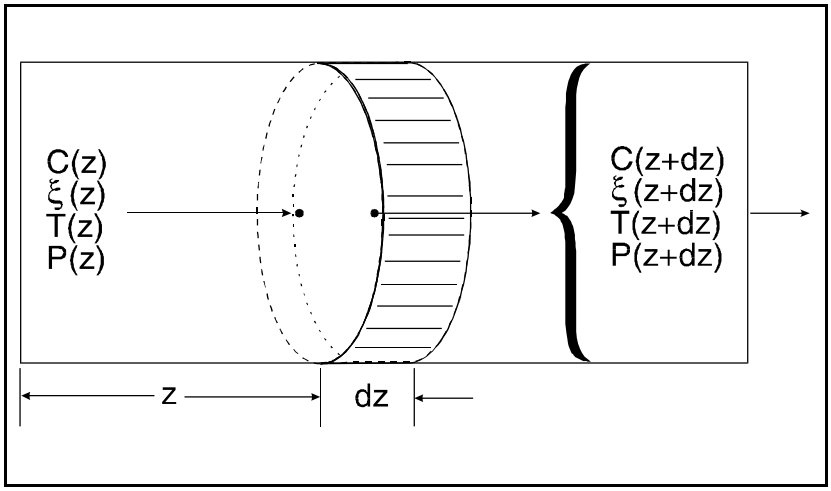


2.6.6 Plug Flow Reactor (PFR)

The plug flow reactor is an idealized model of a tubular reactor. Whereas the feed mixture to a CSTR reactor gets instantaneously mixed, the fluid elements entering the plug flow reactor are assumed to be unmixed in the direction of the flow. Since each element of feed spends the same time in the reactor, the plug flow reactor is also a convenient method of modeling a batch reactor (on a spatial basis instead of on a time variable basis).

A schematic diagram of a plug flow reactor is shown in Figure 2.6.6-1.

Figure 2.6.6-1: Plug Flow Reactor



Design Principles

The steady state mass and energy balance for the one-dimensional PFR for M simultaneous reactions can be derived as follows:

Mass balance:

$$G\frac{d\xi_i}{dz} = \Re_i(\xi_i, \xi_2, ..., \xi_M, P, T) \qquad (1)$$

Energy balance:

$$G\frac{dT}{dz} = J\Re^*(\xi_1, \xi_2, ..., \xi_M, P, T) + Q \qquad (2)$$

where:

G =	mass flow per unit area through the reactor
ξ =	extent of reaction per unit mass
$\Re_i$ =	rate or reaction for the ith reaction
$\Re^*$ =	total reaction rate of whole system
z =	axial distance from the inlet of the reactor
T =	temperature at a distance z from the inlet

$$Q = \frac{Q^*}{\hat{C}_p} \tag{3}$$

Q^* = heat transferred to or from the reactor per unit area

P = pressure

J = heat transfer ratio,

$$= \left(\frac{\Delta H_R}{\hat{C}_p}\right) \tag{4}$$

$\hat{C}_p$ = mean heat capacity of the species in the reactor

ΔH_R = total heat of reaction

Equations (1) and (2) may be combined to eliminate the reaction rate term to give:

$$\frac{dT}{dz} - J\frac{d\xi}{dz} = \frac{Q}{G} \tag{5}$$

or

$$T = T_o + J\xi + \int_0^z \frac{Q}{G} dz \tag{6}$$

where:

$$T = T_0, \quad \xi = 0 \quad at \;\; z = 0 \tag{7}$$

are the initial conditions.

There are now various cases that may arise.

I. Temperature programmed reactor.

(a) Isothermal. If T (z) = T, then equation (1) can be integrated by standard numerical methods.

(b) If T (z) is specified, *i.e.*, a profile for T is given, then equation (1) can be solved by numerical quadratures.

II. Heat control programmed.

(a) Adiabatic. If Q(z) = 0 we have the constancy of (T - Jξ), and equation (1) can be written as a function of ξ only.

(b) If Q(z) $0 \le z \le L$, is specified (profile of heat transfer given), equations (1) and (2) have to be solved simultaneously.

III. Heat control governed by a further equation.

In this case we have to consider the physical form of the cooling or heating supplied. If $T_c(z)$ is the coolant temperature at position z, the heat transfer equation can be written as $Q^* = h^* (T_c - T)$, which leads to another series of sub-cases.

(a) T_c constant. In this case the differential equations for ξ and T can be integrated together. This could also be done if T_c were specified as a function of z.

(b) T_c governed by a further differential equation. Here, the issues to be considered are: the form of coolant flow (cocurrent or countercurrent) and whether the cold feed itself is to be used as the coolant.

PFR Operation Modes

PRO/II allows for the following modes of plug flow reactor operation:

- adiabatic, with or without heat addition/removal
- thermal, with the option of indicating temperature and pressure profiles
- cocurrent flow
- countercurrent flow (the outlet temperature of the cooling stream is required).

The thermal mode of operation is the default.

There are two methods of numerical integration available in PRO/II. The Runge-Kutta method is the default method, and is preferred in most cases. When sharply varying gradients are expected within the reactor, the Gear method, which has a variable integration step size, may be preferred.

For exothermic reactions, two valid solutions (the low conversion and the high conversion) are possible. The plug flow reactor model in PRO/II is not equipped to find the hot spot or ignition temperature. The user can manipulate the exit cooling temperature for countercurrent reactors or stream product temperature for autothermal reactors to get either the low conversion or the high conversion solution.

Reference

Smith, J.M., 1970, 2nd Ed., Chemical Engineering Kinetics, McGraw-Hill, NY.

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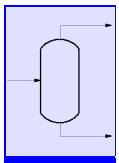
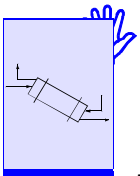


2.7 Solids Handling Unit Operations

The following types of solids handling equipment may be simulated in PRO/II:

- Dryer
- Rotary drum filter
- Filtering centrifuge
- Countercurrent decanter
- Melter/Freezer
- Dissolver
- Crystallizer



2.7.1 Dryer

General Information

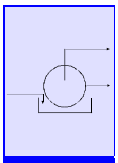
PRO/II has the capability of simulating a simple continuous solids dryer in which the drying gas and solid streams flow countercurrent to each other. The liquid (typically water) content of the solid stream is reduced by contact with the hot gas stream. The dryer unit is simulated in much the same way as the flash drum unit is. If the stream composition and rate are fixed, then there are 2 degrees of freedom that may be fixed. Any one of the following combination of specifications may be used when defining the dryer unit operation:

DRYER OPERATION	SPECIFICATION 1	SPECIFICATION 2
ISOTHERMAL	TEMPERATURE	PRESSURE
ISOTHERMAL	TEMPERATURE	DP
ADIABATIC	TEMPERATURE	FIXED DUTY
	PRESSURE	FIXED DUTY
DESIGN	TEMPERATURE	GENERAL DESIGN SPECIFICATION
DESIGN	PRESSURE	GENERAL DESIGN SPECIFICATION
DESIGN	DP	GENERAL DESIGN SPECIFICATION

A design specification may be the amount of feed vaporized, or the moisture content of the solids product, or a rate or fraction (or PPM) specification on either product stream.

Calculation Methods

The design specification is used along with mass balance equations to calculate the operating dryer temperature or pressure (the other is specified). A two-phase (VL) flash is performed to determine the vapor and liquid phase distributions. The details of the calculation flash algorithm may be found in Section 2.1, *Flash Calculations*.



2.7.2 Rotary Drum Filter

General Information

In solid-liquid separations, horizontal rotary drum filters are often used to decrease the liquid content of a stream containing solids. For a given filter diameter and width (rating calculations), PRO/II will compute the pressure drop, cake thickness, average cake saturation, as well as determine the rates of the solid cake and filtrate product streams. For design calculations, PRO/II will determine the drum diameter and width required for a given pressure drop.

Calculation Methods

As a solid-liquid mixture is filtered, a layer of solid material, known as the filter cake, builds up on the filter surface. Vacuum filtration is used to drain liquid through the filter cake. An important characteristic of the filter cake is its permeability. The permeability is defined as the proportionality constant in the flow equation for laminar flow due to gravity through the bed. The permeability is a function of the characteristics of the cake, such as the sphericity and size of the cake particles and the average porosity of the cake, and is given by:

$$K = g_c \, d_p^2 \, \varepsilon^{(A-B)} \qquad (1)$$

where:

K = permeability of filter cake

g_c = acceleration due to gravity

d_p = diameter of cake particle

ε = average porosity of filter cake

A,B are constants

The values of the constants A and B in equation (1) are a function of $\phi = \frac{\alpha}{\varepsilon}$, the ratio of the particle sphericity to the cake porosity. A and B are given by:

For $\phi > 1.5$,

$$A = \exp(2.49160 - 0.2099\phi)$$

$$B = \exp(1.74456 - 0.2085\phi) \qquad (2\text{-}3)$$

For $\phi < 1.5$,

$$A = \exp\left(1.8780 - \frac{0.4942}{\phi}\right)$$

$$B = \exp\left(1.1069 - \frac{0.5144}{\phi}\right) \qquad (4\text{-}5)$$

The pressure drop across the filter cake is then given by:

$$\Delta P_c = \frac{2L\mu_L S k_c}{\theta D^2 W^2 \varpi A_{tot}^2} \qquad (6)$$

where:

L = liquid volumetric flowrate through the cake

μ_L = liquid viscosity

S = rate of dry solids in the feed

k_c = cake resistance

θ = angle of filtration

D = diameter of filter drum

W = width of filter drum

ϖ = drum rotational speed in rad/s = $2\pi\frac{(RPM)}{60}$

RPM = rotational speed of drum in revolutions/min

A_{tot} = total filter area = $2\pi DW$

The actual pressure drop across the drum filter is then given by:

$$\Delta P_{act} = \Delta P_c^{(1/(1-Cf))} \qquad (7)$$

where:

C_f = filter cake compressibility factor

The value of the filter cake compressibility factor can vary from 0 for an in-compressible cake to 1.0 for a highly compressible cake. Industrially, the value of C_f is typically 0.1 to 0.8.

The filter bed thickness is given by:

$$t = \frac{S}{\varpi D^2 W \rho_s (1-\varepsilon)} \qquad (8)$$

The filter bed will never become completely dry, but will always contain a certain amount of liquid which cannot be removed by filtration. This liquid remains in the spaces between particles, and is held in place by the surface tension of the liquid. This residual cake saturation is a function of a dimensionless group known as the capillary number, N_c. The capillary number is given by:

$$N_c = \frac{K\left(\rho_L + \frac{\Delta P_{act}}{t}\right)}{\sigma} \qquad (9)$$

where:

ρ_L = liquid density

The residual cake saturation, s_0 is calculated based on the value of the capillary number:

For $0.002 < N_C < 0.03$,

$$s_0 = 10^{(-1.8 - 0.299 \log_{10} N_c)} \qquad (10)$$

For $N_C > 0.03$,

$$s_0 = 10^{(-2.759 - 0.957 \log_{10} N_c)} \qquad (11)$$

For $N_C < 0.002$,

$$s_0 = 0.072 \qquad (12)$$

The average level of saturation in the cake is a function of the filter pressure drop as well as cake characteristics such as the cake drain number, drain height, and thickness. The cake drain number and height are calculated from the cake permeability, and the liquid density and surface tension:

$$N_C = \sqrt{K}\,\frac{\rho_L}{\sigma}$$

$$h_D = \frac{0.275}{N_D} \qquad (13\text{-}14)$$

The average cake saturation is given by:

$$s_{av} = \exp\left(-2.993 - 0.036z^2y + 0.055z^2 - 0.274z - 0.756zy - 0.099zy^2 + 0.500y + 0.172y^2 \right) \quad (15)$$

where:

$$z = \frac{t}{h_D}$$

$$y = \ln\left(0.453K^{1/3}\left(1 + \frac{\Delta P_{act}}{t\rho_L} \right)^2 \right) \quad (16\text{-}17)$$

For design calculations, an iterative method solution method is used, in combination with the equations given above, to calculate the filter diameter and width required to produce a specified pressure drop.

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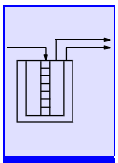
PRO/II Note: For more information on using a rotary drum filter in PRO/II, see Section 102, *Rotary Drum Filter*, of the *PRO/II Keyword Input Manual*.

References

1. Treybal, R. E., 1980, Mass-Transfer Operations, 3rd Ed., McGraw-Hill, N.Y.
2. Dahlstrom, D.H., and Silverblatt, C.E., 1977, Solid/Liquid Separation Equipment Scale Up, Uplands Press.
3. Brownell, L.E., and Katz, D.I., 1947, *Chem. Eng. Prog.*, **43**(11), 601.
4. Dombrowski, H.S., and Brownell, L.E., 1954, *Ind. Eng. Chem.*, **46**(6), 1207.
5. Silverblatt, C.E., Risbud, H., and Tiller, F.M., 1974, *Chem. Eng.*, 127, Apr. 27.



2.7.3 Filtering Centrifuge

General Information

An alternate solid-liquid separating unit to the rotary drum filter is the filtering centrifuge. In this type of unit, the solid-liquid mixture is fed to a rotating perforated basket lined with a cloth or mesh insert. Liquid is forced through the basket by centrifugal force, while the solids are retained in the basket. PRO/II contains five types of filtering centrifuges as indicated in Table 2.7.3-1.

Table 2.7.3-1:
Types of Filtering Centrifuges Available in PRO/II

Type	Description
WIDE	Wide angle. Half angle of basket cone > angle of repose of solids.
DIFF	Differential scroll. Movement of solids from filter basket controlled by a screw.
AXIAL	Axial vibration. High frequency force applied to the axis of rotation.
TORSION	Torsional vibration. High frequency force applied around the drive shaft.
OSCIL	Oscillating. A low frequency force is applied to a pivot supporting the drive shaft.

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PRO/II Note: For more information on specifying the type of filtering centrifuge in PRO/II, see Section 103, *Filtering Centrifuge, of the PRO/II Keyword Input Manual*.

Calculation Methods

For rating applications, the basket diameter, rotational speed in revolutions per minute, and centrifuge type are specified. The centrifugal force is then computed using:

$$g_{cent} = \frac{r\omega^2}{g_c} \qquad (1)$$

where:

g_{cent} = centrifugal force

r = radius of centrifuge basket

$\omega = \frac{2\pi(RPM)}{60}$ = rotational speed, rad/s

RPM = rotational speed of basket in revolutions/min

g_c = acceleration due to gravity

The amount of solids remaining the basket is computed from:

$$M_s = \pi\left(r^2 - r_{cake}^2\right)h\rho_s\,(1-\varepsilon) \qquad (2)$$

where:

M_s = mass of solids remaining in the basket
r_{cake} = radius of inner surface of filter cake
h = height of basket
ρ_s = solid density
ε = average filter cake porosity

The thickness of the filter cake is given by:

$$t_{cake} = r - r_{cake} \qquad (3)$$

The surface area of the filter basket, and the log-mean and arithmetic mean area of the filter cake are given by:

$$A_{cake,lm} = \frac{2\pi h t_{cake}}{\ln(r / r_{cake})}$$

$$A_{cake,mean} = \pi(r + r_{cake})h$$

$$A_{filter} = 2\pi r h \qquad (4\text{-}6)$$

where:

$A_{cake,lm}$ = log-mean surface area of filter cake
$A_{cake,mean}$ = arithmetic mean surface area of filter cake
A_{filter} = surface area of filter basket

The drainage of liquid through the filter cake of granular solids in a filtering centrifuge is a result of two forces; the gravitational force, and the centrifugal force in the basket, and is given by:

$$K = d_p^2\,\varepsilon^{(A-B)} \qquad (7)$$

where:

K = permeability of filter cake
d_p = diameter of cake particle
A,B are constants

The values of the constants A and B in equation (7) are a function of $\phi = \frac{\alpha}{\varepsilon}$, the ratio of the cake sphericity to the cake porosity. A and B are given by:

For $\phi > 1.5$,

$$A = \exp(2.49160 - 0.2099\phi)$$

$$B = \exp(1.74456 - 0.2085\phi) \quad (8\text{-}9)$$

For $\phi < 1.5$,

$$A = \exp\left(1.8780 + \frac{0.4942}{\phi}\right)$$

$$B = \exp\left(1.1069 + \frac{0.5144}{\phi}\right) \quad (10\text{-}11)$$

The residual cake saturation, a result of small amounts of liquid held between the cake particles by surface tension forces, is a function of a dimensionless group known as the capillary number, N_c. The capillary number is given by:

$$N_c = \frac{K \rho_L g_{cent}}{g_c \sigma} \quad (12)$$

where:

ρ_L = liquid density

σ = liquid surface tension

The residual cake saturation, s_0 is then calculated based on the value of the capillary number:

For $0.002 < N_c < 0.03$,

$$s_0 = 10^{(-1.8 - 0.299 \log_{10} N_c)} \quad (13)$$

For $N_c > 0.03$,

$$s_0 = 10^{(-2.759 - 0.957 \log_{10} N_c)} \quad (14)$$

For $N_c < 0.002$,

$$s_0 = 0.072 \quad (15)$$

The cake drain number and height are calculated from the cake permeability, centrifugal force, and the liquid density and surface tension:

$$N_D = \sqrt{\frac{K}{g_c}} \frac{\rho_L g_{cent}}{\sigma}$$

$$h_d = \frac{0.275}{N_D} \quad (16\text{-}17)$$

The average cake saturation is then given by:

$$s_{av} = s_0 \left[\frac{t_{cake} - h_D}{t_{cake}} \right] - \frac{h_D}{t_{cake}} \qquad (18)$$

where:

s_{av} = average filter cake saturation

The corresponding moisture content of the filter cake, X_{cake}, is calculated using:

$$X_{cake} = s_{av} \left[\frac{\varepsilon}{1-\varepsilon} \right] \frac{\rho_L}{\rho_s} \qquad (19)$$

Finally, the actual rate of filtrate through the basket is given by:

$$F_{filtr} = \frac{\left\{ F_{feed} (w_{liq} - w_{sol}) + F_{inert} \right\} X_{cake}}{\rho_L} \qquad (20)$$

where:

F_{filtr} = rate of filtrate
F_{feed} = total mass rate of feed to centrifuge
w_{liq} = weight fraction of liquid in feed
w_{sol} = weight fraction of solid in feed
F_{inert} = total mass rate of inert components in feed

For design calculations, an iterative method solution method is used, in combination with the equations given above, to calculate the filter diameter required to produce a specified filtrate flow.

References

1. Treybal, R. E., 1980, Mass-Transfer Operations, 3rd Ed., McGraw-Hill, N.Y.
2. Grace, H.P., 1953, *Chem. Eng. Prog.*, **49**(8), 427.
3. Dombrowski, H.S., and Brownell, L.E., 1954, *Ind. Eng. Chem.*, **46**(6), 1207.

2.7.4 Countercurrent Decanter

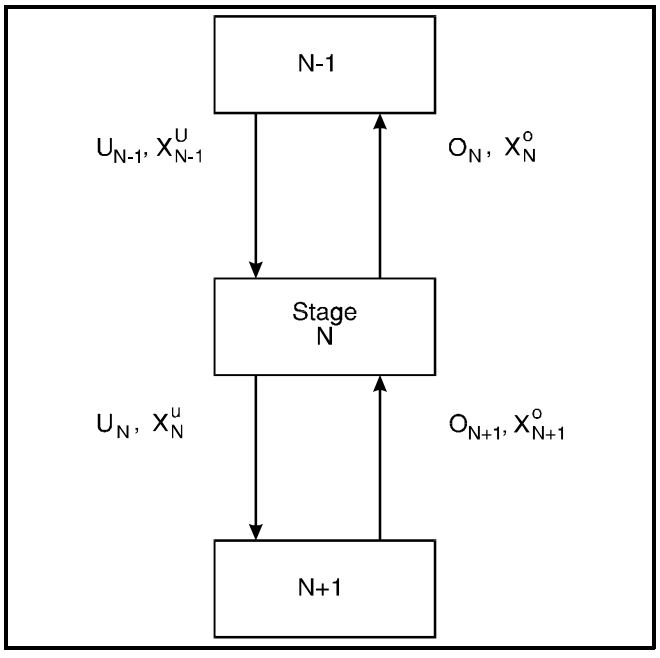
General Information

Mixtures of solids and liquids may be separated by countercurrent decantation (CCD). This unit operation consists of several settling tanks in series. If the purpose of the CCD unit is to obtain a thickened underflow, then the tank is referred to as a thickener. The solid-liquid mixture is flowed countercurrently to a dilute liquid wash stream. In each tank, the solids from the slurry feed settles under gravity to the bottom of the tank. The clarified overflow is transferred to the previous tank to be used as the wash liquid, while the underflow from the tank is transferred to the next tank in the series. The feed to the first tank in the series therefore consists of the slurry feed and the overflow from the second tank, while the feed to the last tank consists of the liquid wash (typically water), and the underflow slurry from the second to last tank. If the purpose of the CCD unit is to obtain a clear overflow, then the tank is referred to as a clarifier.

Calculation Methods

A typical stage of the countercurrent decantation system is shown in Figure 2.7.4-1.

Figure 2.7.4-1: Countercurrent Decanter Stage



The equations describing the model are as developed below.

Total Mass Balance:

$$U_N = TS / PS$$

$$O_N = U_{N-1} + O_{N+1} - U_N \qquad (1\text{-}2)$$

where:

U = decanter underflow rate from a stage

PS = solid fraction in underflow

TS = total solids flow through CCD

O = total overflow rate from a stage

subscripts N, $N\text{-}1$, $N+1$ refer to stage N, and the stages below and above stage N

Component Balance:

$$x^U_{i,N-1}\, U_{N-1} + x^O_{i,N+1}\, O_{N+1} = U_N\, x^U_{i,N} + O_N x^O_{i,N} \qquad (3)$$

where:

x^U = composition of underflow from a stage

x^O = composition of overflow from a stage

The mixing efficiency for each stage, E_N, is given by:

$$E_N = \frac{x^U_{i,N-1}}{x^O_{i,N}} \qquad (4)$$

The mixing efficiency is generally a function of temperature and composition. However, in PRO/II, it is assumed that the mixing efficiency is constant for each stage. This assumption, along with the fixing of the ratio of the overflow solids concentration to the underflow solids concentration, decouples the solution of equations (1-4), and enables the equations to be solved simultaneously. Equations (1-4) may be re-written as:

$$b_1 x^U_{i,1} + \delta_1\, x^U_{i,2} = F_{i,1}\,, \quad \textit{for stage 1} \qquad (5)$$

$$\alpha_N\, x^U_{i,N-1} + \beta_N\, x^U_{i,N} + \delta_N\, x^U_{i,N+1} = F_{i,N}\,, \quad \textit{for stages 2 to N-1} \qquad (6)$$

$$\alpha_N\, x^U_{i,N-1} + \beta_N\, x^U_{i,N} = F_{i,N}\,, \quad \textit{for stage N} \qquad (7)$$

where:

$$\beta_1 = \frac{U_1 + O_1 R_1 - \dfrac{(R_2 - 1)\, O_2 U_1}{Y_1}}{D_1} \qquad (8)$$

$$\delta_1 = \frac{O_2 R_2}{D_1} \quad (9)$$

$$F_{i,1} = \frac{F_1^C f_{i,1}^C}{D_1} \quad (10)$$

$$D_1 = O_1 (R_1 - 1) \quad (11)$$

$$\alpha_N = -1 \quad (12)? \quad (13)$$

$$\beta_N = \frac{U_N + O_N R_N - \frac{(R_{N+1} - 1) O_{N+1} U_N}{y_N}}{D_N}$$

$$y_N = U_N \quad (14)$$

$$\delta_N = \frac{O_{N+1} R_{N+1}}{D_N} \quad (15)$$

$$F_{i,N} = \frac{F_N^C f_{i,N}^C}{D_N} \quad (16)$$

$$D_N = U_{N-1} - (R_N - 1) O_N \quad (17)$$

$$R_N = \frac{1}{E_N} \quad (18)$$

The underflow and overflow stream temperatures from each stage are the same and are assumed equal to the stage temperature, i.e., the stage is in thermal equilibrium.

Calculation Scheme

For the rating calculations, the total mass balances are solved easily once the total solids and percent solids underflow at each stage are specified. The calculation procedure is given below.

- First the underflow rates are calculated from equation (1). The wash water rate to the last stage is known, and the last stage overflow rate is then calculated using:

$$O_N = F_2 + U_{N-1} - U_N \quad (19)$$

- The remaining overflow rates are then calculated from the last stage backwards to the first stage using equation (2).
- Once U_N and O_N are calculated for all stages, the component balance equations are then solved using the Thomas algorithm, a version of the Gaussian elimination procedure. This method of solving the triagonal equations (5-7) avoids matrix inversion, buildup of truncation errors, and avoids negative values of $x_{i,N}$ being produced. The triagonal equations can be reduced to:

$$\begin{bmatrix} 1 & p_1 & 0 & 0 & \cdots & 0 \\ 0 & 1 & p_2 & 0 & \cdots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdots & \cdot \\ 0 & 0 & 0 & 0 & \cdots & p_{N-1} \\ 0 & 0 & 0 & 0 & \cdots & 1 \end{bmatrix} \begin{bmatrix} x_{i,1} \\ x_{i,2} \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ x_{i,N-1} \\ x_{i,N} \end{bmatrix} = \begin{bmatrix} q_{i,1} \\ q_{i,2} \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ q_{i,N-1} \\ q_{i,N} \end{bmatrix} \quad (20)$$

where:

$$p_1 = \frac{\delta_1}{\beta_1} \quad (21)$$

$$q_{i,1} = \frac{F_{i,1}}{\beta_1} \quad (22)$$

$$p_N = \frac{\delta_N}{\beta_N - \alpha_N p_{N-1}} \quad (23)$$

$$q_{i,N} = \frac{F_{i,N} - \alpha_N q_{N-1}}{\beta_N - \alpha_N p_{N-1}} \quad (24)$$

The solution of this matrix results in the immediate solution of the last stage composition $x_{i,N}$, using the last row of the matrix, i.e.,

$$x_{i,N} = q_{i,N} \quad (25)$$

The compositions on other stages are then obtained by backward substitution:

$$x_{i,N-1} = q_{i,N-1} - p_{N-1}\, x_{i,N} \quad (26)$$

For the design mode calculations, the number of stages is not given, but a recovery specification is made on either the overhead or underflow product. In this case, PRO/II will begin the calculations described above by assuming a minimum number of stages present. If the design specification is not met, the number of stages will be increased, and the design equations re-solved until the specification is met.

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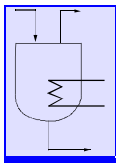
PRO/II Note: For more information on specifying limits on the number of stages when running in design mode, see Section 104, *Countercurrent Decanter*, of the *PRO/II Keyword Input Manual*.

Reference

Scandrett, H.E., Equations for Calculating Recovery of Soluble Values in a Countercurrent Decantation Washing System, 1962, *Extractive Metallurgy of Aluminum*, **1**, 83



2.7.5 Dissolver

General Information

Dissolution of solids into liquid solutions is a mass transfer operation which is widely used in the chemical industry in both organic as well as inorganic processes. A unit operation that utilizes mass transfer controlled dissolution is the stirred tank dissolver. The contents of the stirred tank dissolver are well-mixed using an agitator, and when it is operated in a continuous manner, the unit can be called a continuous stirred tank dissolver or CSTD. The PRO/II dissolver is of the CSTD type.

Development of the Dissolver Model

The dissolution of a solute from the solid particle into the surrounding liquid can be modeled as the rate of decrease in volume of the solid particle:

$$\rho_p\left(V_P\mid_t - V_p\mid_{t+\Delta t}\right)=\left(A_p k_L\,(\rho_L\,S-C)\right)\Delta t \qquad (1)$$

where:

ρ_p = density of solid particle, kg/m^3
V_p = volume of particle, m^3
A_p = surface area of particle, m^2
k_L = liquid phase mass transfer coefficient, kg/m^2-sec
ρ_L = liquid density, kg/m^3
S = solubility, kg solute/kg liquid
C = liquid phase concentration of solute, kg/m^3
t = time, sec

As $\Delta t \rightarrow 0$, equation (1) becomes:

$$\rho_p \frac{dVp}{dt} = A_p k_L\,(\rho_L\,S-C) \qquad (2)$$

$$V_p = \frac{4}{3}\pi r^3,\ A_p = 4\pi r^2 \qquad (3)$$

where:

r = radius of solid particle, m

and

$$\rho_p \frac{dr}{dt} = k_L\,(\rho_L\,S-C) \qquad (4)$$

Equation (4) describes the mass transfer rate per unit area as dependent on two factors; the mass transfer coefficient and concentration difference. The mass transfer coefficient is the liquid phase coefficient, since diffusion of the solute from the particle surface through the liquid film to the bulk of the liquid solution is the dominant or rate-controlling step. The concentration difference is the difference between the equilibrium concentration at the solid-liquid interface and the solute concentration in the dissolver liquid.

Integrating equation (4) for constant k_L,

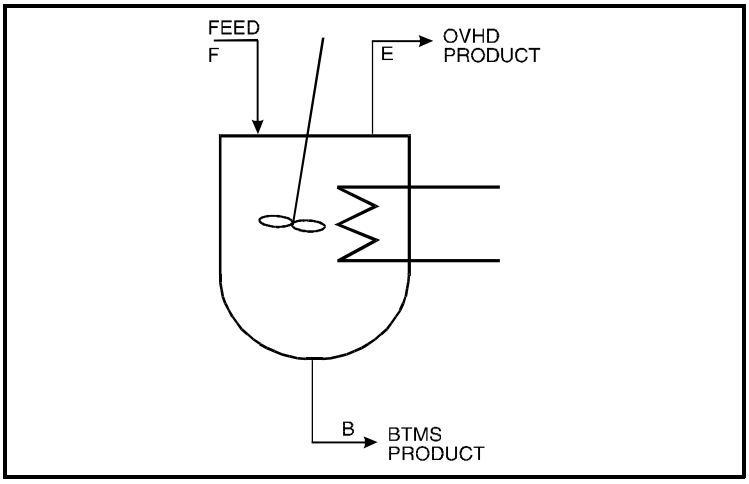
$$\Delta r = \frac{k_L}{\rho_p}(\rho_L S - C)\,\tau \qquad (5)$$

represents the change in particle size due to the dissolution process.

The following simplifying assumptions are used in the development of the dissolver model:

- The solid particles are spherical in shape.
- There is no settling, breakage, or agglomeration of solid particles.
- The liquid in the dissolver follows a continuous stirred tank type flow, whereas the solid particles are in plug flow. As a result, the temperature and liquid phase concentration in the dissolver are uniform, and all the solid particles have the same residence time.
- The dissolution of a single solid component only is modeled, and the presence of ''inert'' components has no effect on the dissolution process.

Figure 2.7.5-1: Continuous Stirred Tank Dissolver



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PRO/II Note: For information on using dissolvers in PRO/II, see Section 105, *Dissolver*, of the *PRO/II Keyword Input Manual* and the *PRO/II Applications Briefs Manual*, S1: *p-Xylene Crystallization*.

Mass Transfer Coefficient Correlations

The liquid phase mass transfer coefficient k_L is a function of various quantities such as diffusivity of solute in liquid solution, impeller power and diameter, and physical properties of the solid component and liquid. For large particles, the coefficient has been found to be independent of particle size, whereas for smaller particles, the coefficient increases with decreasing particle size.

The following correlation has been proposed by Treybal for liquid phase mass transfer in solid-liquid slurries:

For $d_p < 2$ mm,

$$Sh_L = 2 + 0.47\ \mathrm{Re}_p^{0.62}\left(\frac{d_i}{d_t}\right)^{0.17} Sc_L^{0.36} \qquad (6)$$

For $d_p > 2$ mm,

$$Sh_L = 0.222\ \mathrm{Re}_p^{3/4}\, Sc_L^{1/3} \qquad (7)$$

where:

d_p = solid particle diameter, m

Sh_L = liquid phase Sherwood number, dimensionless

Re_p = particle Reynolds number, dimensionless

d_i = impeller diameter, m

d_t = dissolver tank diameter, m

Sc_L = liquid phase Schmidt number, m

This is the default correlation used in the dissolver model for calculating the mass transfer coefficient.

If detailed mass transfer data are available, the following correlation can be selected by specifying the parameters a,b, and d_{cut}:

For $d_p < d_{cut}$,

$$k_L = \frac{a}{d_p} + \frac{b}{d_p^{0.1733}} \qquad (8)$$

where:

a,*b* are mass transfer coefficient parameters

d_{cut} = solid particle cut-off diameter, m

When the mass transfer coefficient is a function of particle size, equation (4) can be integrated as:

$$\int_{r_i}^{r_2} \frac{dr}{k_L} = \tau\,(\rho_L S - C)/\rho_p \qquad (9)$$

using numerical quadrature.

Note: Both r (radius) and d_p (diameter) are used for particle size here, but interconversion between r and d_p is done in the program.

Particle Size Distribution

For a solid represented by a discrete particle size distribution, r_{1f}, r_{2f}, ...r_{if} and m_{1f}, m_{2f}, ... m_{if} are the particle sizes and mass flowrates of the feed solids, and r_{1p}, r_{2p}, ... r_{ip} is the particle size distribution of the solids in the product.

For the case of constant k_L, from equation (5),

$$r_{ip} = r_{if} - \frac{k_L}{\rho_p}(\rho_L S - C)\tau \qquad (10)$$

and the rate of dissolution is:

$$\Phi = \sum_i \left[1 - \left(\frac{r_{ip}}{r_{if}} \right)^3 \right] m_{if} \qquad (11)$$

$$= \sum_i \left[1 - \left(1 - \frac{k_L}{\rho_p r_{if}} (\rho_L S - C(\phi))\, \tau\, (\phi) \right)^3 \right] m_{if}$$

Material and Heat Balances and Phase Equilibria

Material and heat balances around the dissolver as well as vapor-liquid equilibrium have to be satisfied. The equilibrium solid solutility, S, is also determined. These equations, many of them in simplified form, are given below:

Material and Heat Balance Equations

Overall,

$$F = E + B \qquad (12)$$

where:

F = mass rate of feed, kg/sec
E = mass rate of overhead product, kg/sec
B = mass rate of bottoms product, kg/sec

Component,

solute,

$$F_{solute} = E_{solute} + B_{solute} \qquad (13)$$

solvent,

$$F_{solvent} = E_{solvent} + B_{solvent} \qquad (14)$$

inerts,

$$F_i = E_i + B_i,\ i = 1,2...,N \qquad (15)$$

where:

solute refers to the solute component
solvent refers to the solvent component
i refers to the inert component

Solid-liquid Solute Balance,

$$F_{solute} = F_{solute}^{Liq} + P_F \quad (16)$$

$$B_{solute} = B_{solute}^{Liq} + P \quad (17)$$

where:

F_{solute}^{Liq} = mass rate of solute component in feed liquid, kg/sec

P_F = mass rate of solid in feed, kg/sec

B_{solute}^{Liq} = mass rate of solute component in bottoms product liquid, kg/sec

P = mass rate of solid in bottoms product, kg/sec

Solute Vapor Balance,

$$E_{solute} = Y_{solute}\left(\frac{E}{MW_{vapor}}\right)MW_{solute} \quad (18)$$

where:

MW_{solute} = molecular weight of solute component kg/kgmol

MW_{vapor} = molecular weight of overhead product, kg/kgmol

E = mass rate of overhead product, kg/sec

Y = mole fraction in overhead product

Heat Balance Equation,

$$Heat\ Duty = Product\ Enthalpy - Feed\ Enthalpy \quad (19)$$

Phase Equilibrium Equations

Solid-liquid Equilibrium,

$$X_{solute} = f_1\ (temperature) \quad (20)$$

Vapor-liquid Equilibrium,

$$Y_i = f_2\ (X_i) \quad (21)$$

Residence Time,

$$\tau = V / Q \quad (22)$$

where:

τ = residence time in the dissolver, sec

V = operating volume of the dissolver, m^3

Q = volumetric rate of bottoms product, m^3/sec

Concentration,

$$C = C_f - \Phi / Q \qquad (23)$$

Solution Procedure

The solution procedure or algorithm using the above equations performs sequential calculations of the solid-liquid problem through mass transfer kinetics and vapor-liquid equilibrium calculations along with heat and material balances. This iteration loop is repeated until product stream compositions do not change and convergence is obtained.

References

1. Parikh, R., Yadav, T., and Pang, K.H., 1991, Computer Simulation and Design of a Stirred Tank Dissolver, Proceedings of the European Symposium on Computer Applications in Chemical Engineering, Elsevier.
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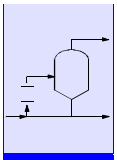


2.7.6 Crystallizer

General Information

The crystallizer is used for separation through the transfer of the solute component from a liquid solution to the solid phase. The crystallization process depends on both phase equilibria as well as kinetic or nonequilibrium considerations.

Solid-liquid equilibrium is defined in terms of solubility, which is the equilibrium composition of the solute in a liquid solution containing the solvent component. Solubility is a function of temperature, and is calculated from either the van't Hoff equation or user-supplied solubility data. The solubility is rigorously calculated if electrolyte thermodynamic methods are used. Crystallization can occur only in a supersaturated liquid solution. A supersaturated liquid is one in which the solute concentration exceeds the equilibrium solubility at the crystallizer temperature. Supersaturation is generally created by cooling the liquid and/or evaporation of the solvent. Additionally, for crystallization systems where evaporation of solvent occurs, the vapor phase and liquid solution satisfy vapor-liquid equilibrium.

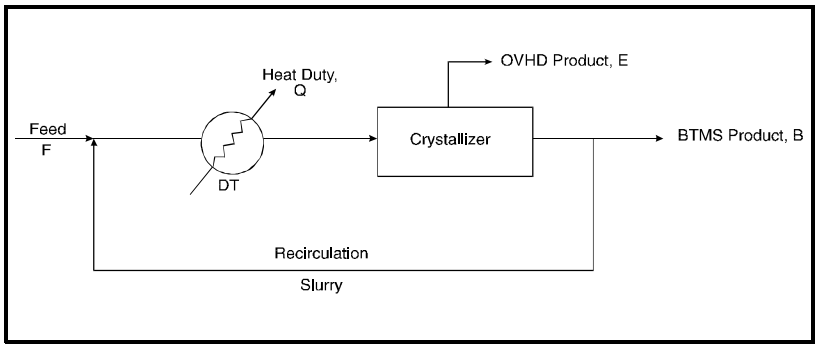
26.1, 26.2

PRO/II Note: For more information on using the van't Hoff and user-supplied solubility methods, see Section 26.1, *van't Hoff Solubility*, and 26.2, *User-supplied Solubility*, in the *PRO/II Keyword Input Manual*.

The quantity of crystals formed depends on the residence time in the crystallizer and is determined by the kinetics of the crystallization process. Crystals are generated from supersaturated solutions by formation of nuclei and by their growth. The primary driving force for both nucleation and crystal growth is the degree of supersaturation. In addition, nucleation is also influenced by mechanical disturbances such as agitation, and the concentrations and growth of solids in the slurry. These rate relationships are normally expressed as power law expressions, which are similar to equations for power law kinetics used for chemical reactions. The constants in the two rate equations are the nucleation rate constant and growth rate constant.

The heat effect associated with the crystallization process is obtained from the input value of the heat of fusion of the solute component. This, along with the enthalpies of the feed and product streams, will determine the heating/cooling duty required for the crystallizer. This duty is generally provided by an external heat exchanger across which a ΔT is maintained. The feed consisting of the fresh feed and recycled product slurry is circulated through the heat exchanger to the crystallizer. If the external heat exchanger option is not turned on in the input file, the duty is assumed to be provided by an internal heater/cooler.

Figure 2.7.6-1: Crystallizer



All crystallizers have some degree of mixing supplied by an agitator and/or pumparound. The limiting case is ideal mixing, where conditions in the crystallizer are uniform throughout, and the effluent conditions are the same as those of the crystallizer contents. Such a unit is commonly known by the name of Mixed Suspension Mixed Product Removal (MSMPR) crystallizer or Continuous Stirred Tank Crystallizer (CSTC). A further assumption made in the development of the crystallizer model is that breakage or agglomeration of solid particles is negligible.

Crystallization Kinetics and Population Balance Equations

Growth Rate:

$$G = k_G S^{GEXP} \qquad (1)$$

where:

G = growth rate of crystals, m/sec

k_G = growth rate constant, m/sec

S = supersaturation ratio = $\dfrac{X_{solute} - X_{solute}^{eq}}{X_{solute}^{eq}}$

X_{solute} = actual mole fraction of solute in liquid

X_{solute}^{eq} = equilibrium mole fraction of solute in liquid at the crystallizer temperature

Nucleation Rate:

$$B_o = \left(k_B M_T^{BEXP1}\right)\left(S^{BEXP2}\right)\left(G^{BEXP3}\right)\left(RPM^{BEXP4}\right) \qquad (2)$$

where:

B_o = crystal nucleation rate, number/sec.m^3

k_B = nucleation rate constant

M_T = magma density, i.e., concentration of crystals in slurry, kg crystals/m^3 slurry

RPM = impeller speed, revolutions/min

BEXP1, BEXP2, BEXP3, BEXP4 = exponents

Nucleii Number Density:

$$n_o = \varepsilon \frac{B_o}{G} \qquad (3)$$

where:

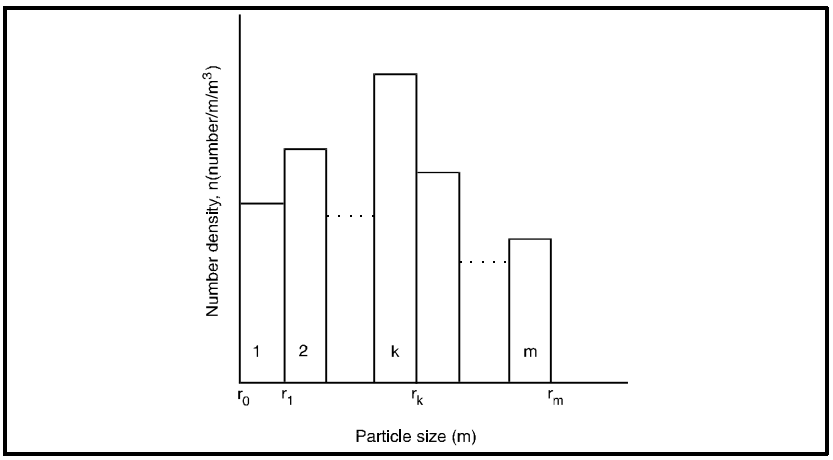
n_o = nucleii number density, number/m/m^3 slurry

ε = liquid volume fraction in slurry, m^3 liquid/m^3 slurry

Population Balance Equations:

For discrete particle size distribution for crystals, number density n(r) can be expressed as a histogram with m divisions and r_k as the average particle size of the kth division.

Figure 2.7.6-2: Crystal Particle Size Distribution



Making a balance on the number density of the crystals in the crystallizer,

$$q_f n_f - qn = GV\frac{dn}{dr} \qquad (4)$$

where:

q = volumetric rate of bottoms product slurry, m^3/sec

q_f = volumetric rate of feed, m^3/sec

V = operating volume of crystallizer, m^3

r = characteristic length of crystal, m

Residence time is defined as:

$$\tau = \frac{V}{q}$$

By rearranging equation (4), multiplying by the integrating factor $e^{r/G\tau}$, and integrating, we get:

$$\int d\left(e^{\frac{r}{G\tau}}n\right)=\frac{q_f}{q}\frac{1}{G\tau}\int n_f e^{\frac{r}{G\tau}}dr \qquad (5)$$

For the k^{th} division,

$$n(r_k)=n(r_{k-1})\frac{e^{r_{k-1}-r_k}}{G\tau}+\frac{q_f}{q}n_{f,k}\left(1-e^{\frac{r_{k-1}-r_k}{G\tau}}\right) \qquad (6)$$

Using the initial condition: $n(r_o) = n_o$ at $r_o = 0$,

$$k=1,\ n(r_1)=n_o e^{\frac{-r_1}{G\tau}}+\frac{q_f}{q}n_{f,1}\left(1-e^{\frac{-r_1}{G\tau}}\right) \qquad (7)$$

$$k=2,\ n(r_2)=n,\ e^{\frac{r_1-r_2}{G\tau}}+\frac{q_f}{q}n_{f,2}\left(1-e^{\frac{r_1-r_2}{G\tau}}\right)$$

$$=\left[n_o e^{-\frac{r_1}{G\tau}}+\frac{q_f}{q}n_{f,1}\left(1-e^{-\frac{r_1}{G\tau}}\right)\right]e^{\frac{r_1-r_2}{G\tau}}+\frac{q_f}{q}n_{f,2}\left(1-e^{\frac{r_1-r_2}{G\tau}}\right)$$

$$=n_o e^{-\frac{r_2}{G\tau}}+\frac{q_f}{q}\left[n_{f,1}\left(e^{\frac{r_1-r_2}{G\tau}}-e^{-\frac{r_2}{G\tau}}\right)+n_{f,2}\left(1-e^{\frac{r_1-r_2}{G\tau}}\right)\right] \qquad (8)$$

For any k, the generalized expression is:

$$n(r_k)=n_o e^{-\frac{r_k}{G\tau}}+\frac{q_f}{q}\sum_{l=1}^{k}n_{f,1}\left(e^{\frac{r_1-r_k}{G\tau}}-e^{\frac{r_{l-1}-r_k}{G\tau}}\right) \qquad (9)$$

For feed containing no solids, equation (9) simplifies to:

$$n(r_k)=n_o e^{-\frac{r_k}{G\tau}} \qquad (10)$$

The magma density, M_T (the weight concentration of crystals in slurry) is calculated from the third moment of the particle size distribution,

$$M_T=\rho_c k_v\int_0^\infty r^3 n dr \qquad (11)$$

where:

ρ_c = density of crystals, kg crystal/m^3 crystal

k_v = crystal shape factor = 1 for cubic crystals, $\pi/6$ for spherical crystals

For the case of no solids in feed, the magma density is:

$$M_T = 6\rho_c k_v n_o (G\tau)^4 \quad (12)$$

Material and Heat Balances and Phase Equilibria

These equations are given in simplified form below:

Material and Heat Balance Equations

Overall,

$$F = E + B \quad (13)$$

where:

F = feed rate, kg/sec

E = overhead product rate, kg/sec

B = bottom product rate, kg/sec

Component,

$$Solute:\ F_{solute} = E_{solute} + B_{solute} \quad (14)$$

$$Solvent:\ F_{solvent} = E_{solvent} + B_{solvent} \quad (15)$$

$$Inerts:\ F_i = E_i + B_i,\ i = 1,2..., N \quad (16)$$

where:

subscripts *solute*, *solvent*, and *i* refer to the solute, solvent and inert components respectively

Solid-liquid Solute Balance,

$$F_{solute} = F_{solute}^{Liq} + P_F^c \quad (17)$$

$$B_{solute} = B_{solute}^{Liq} + P^c \quad (18)$$

where:

F_{solute}^{Liq} = component rate of solute in feed liquid, kg/sec

P_F^c = component rate of solute in crystallizer feed, kg/sec

B_{solute}^{Liq} = component rate of solute in bottoms product liquid, kg/sec

P^c = rate of solute component crystals in bottoms product, kg/sec

Solute Vapor Balance,

$$E_{solute} = Y_{solute}\left(\frac{E}{MW_{vapor}}\right)MW_{solute} \quad (19)$$

where:

Y_{solute} = vapor phase mole fraction of solute

MW_{vapor} = molecular weight of overhead product, kg/kgmol

MW_{solute} = molecular weight of solute, kg/kgmol

Heat Balance Equation,

$$Heat\ Duty = Product\ Enthalpy - Feed\ Enthalpy \quad (20)$$

Phase Equilibrium Equations

Solid-liquid Equilibrium,

$$X^{eq}_{solute} = f_1\ (temperature) \quad (21)$$

where:

X^{eq}_{solute} = equilibrium mole fraction of solute in crystallizer liquid at crystallizer temperature

Vapor-liquid Equilibrium,

$$Y_i = f_2\ (X_i) \quad (19)$$

where:

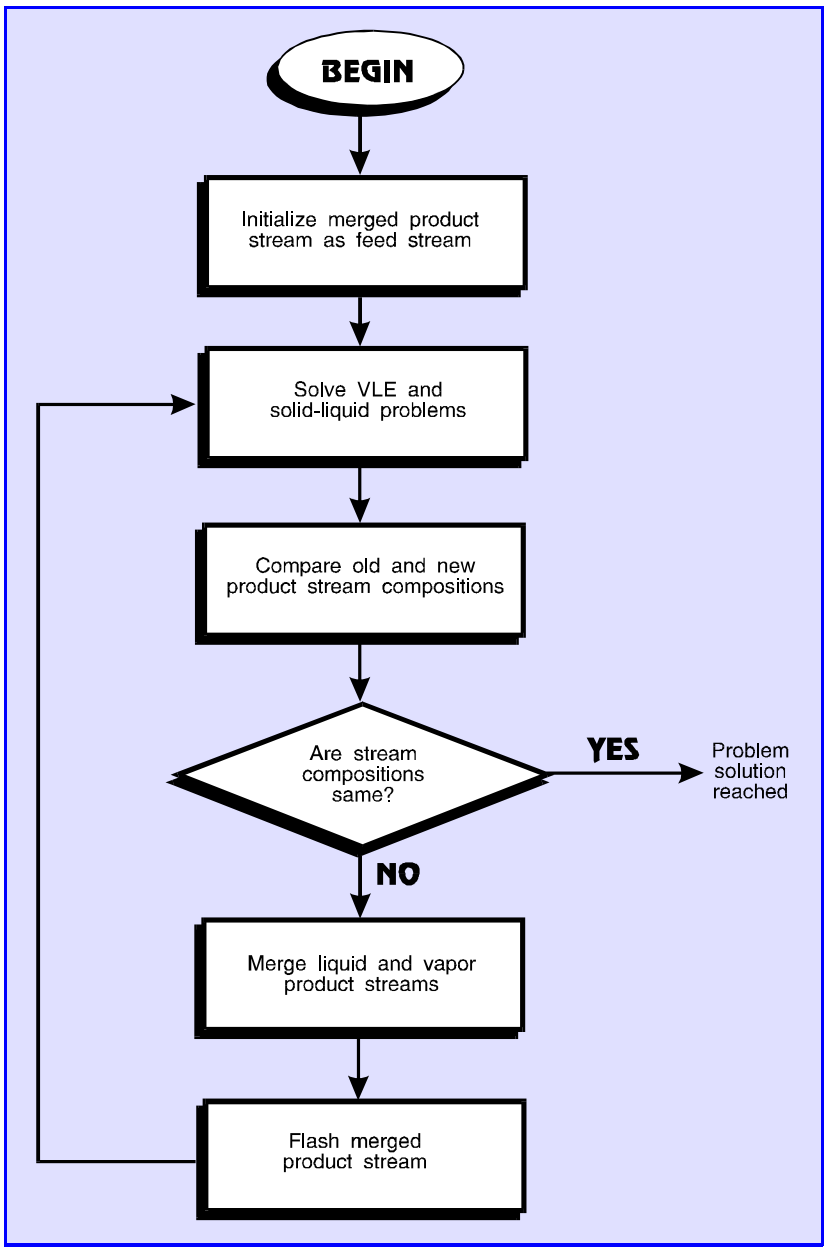
Y_i = vapor phase mole fraction of component i

X_i = liquid phase mole fraction of component i

Solution Procedure

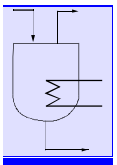
The solution procedure for the crystallizer model uses the above equations to perform solid-liquid calculations through crystallization kinetics in a super-saturated liquid solution, and VLE calculations, along with material balances. The algorithm used is shown in Figure 2.7.6-3.

Figure 2.7.6-3: MSMPR Crystallizer Algorithm



Reference

Treybal, R.E., 1980, Mass Transfer Operations, 3rd Ed., McGraw Hill, N.Y.



2.7.7 Melter/Freezer

General Information

Solid melting and freezing units are important operations in many industries, including food, glass, and edible oil manufacture. Solid components in a mixture may be melted and transformed into a liquid component, and liquid components may be frozen and transformed into solids in the PRO/II melter/ freezer unit operation.

Calculation Methods

The operating temperature and pressure of the melter/freezer is specified by the user. The unit may operate in one of two modes:

- The temperature is specified and PRO/II determines which components are to undergo phase transformation based on the normal melting temperature of each component
- The component and fraction to be frozen or melted is specified. This is the only criteria used for determining which components undergo phase transformation. The melting temperature is ignored for the calculations, and components not specifically given by the user do not undergo a solid-liquid phase change.

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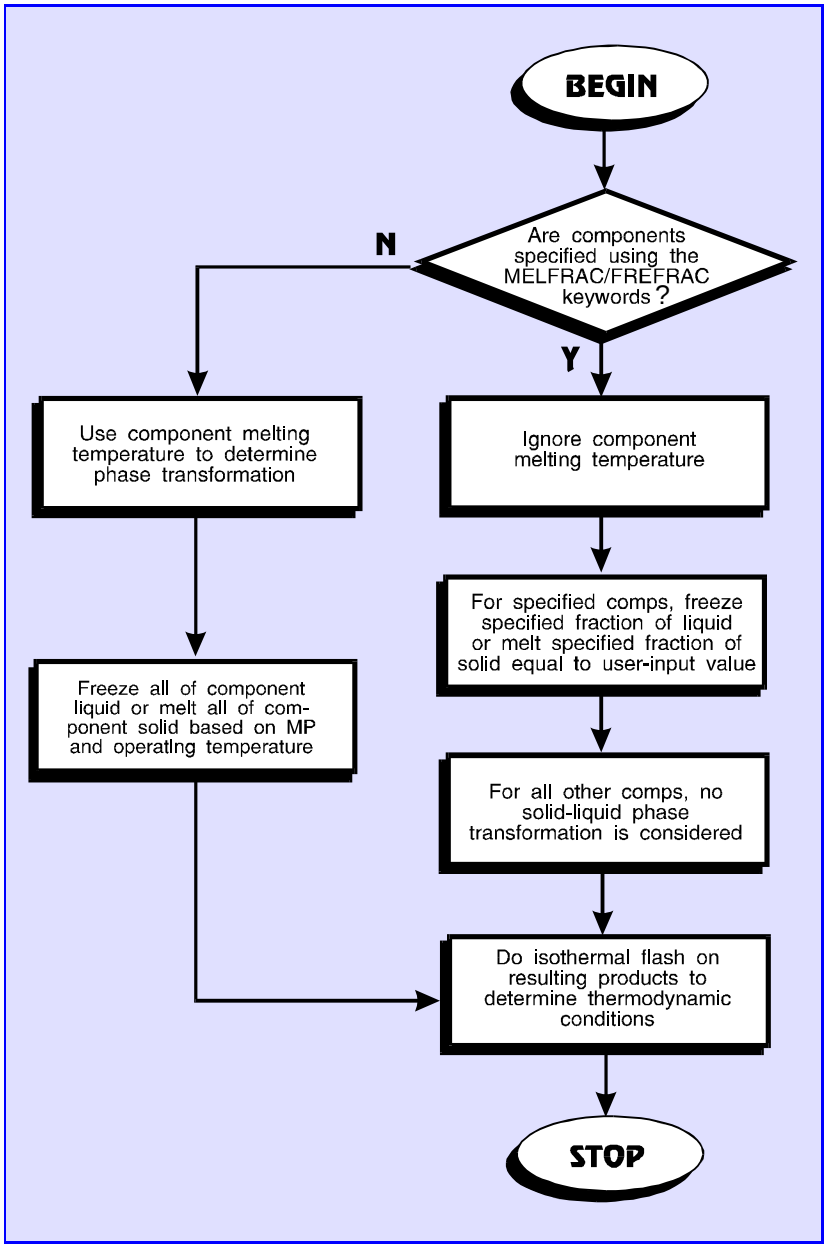
PRO/II Note: For more information on specifying components undergoing phase transformation using the MELFRAC/FREFRAC keyword on the OPERATION statement, see Section 107, *Melter/Freezer*, of the *PRO/II Keyword Input Manual*.

The resulting product streams are then flashed isothermally at the given temperature and pressure conditions to determine their thermodynamic properties. Only the distribution between vapor and liquid (and/or water) phases is considered in the flash calculations. True solid-liquid equilibrium is not considered.

The calculation scheme for this unit operation is shown in Figure 2.7.7-1.

Figure 2.7.7-1: Calculation Scheme for Melter/Freezer


BEGIN
Are components specified using the MELFRAC/FREFRAC keywords ?
N
Y
Use component melting temperature to determine phase transformation
Ignore component melting temperature
For specified comps, freeze specified fraction of liquid or melt specified fraction of solid equal to user-input value
Freeze all of component liquid or melt all of component solid based on MP and operating temperature
For all other comps, no solid-liquid phase transformation is considered
Do isothermal flash on resulting products to determine thermodynamic conditions
STOP

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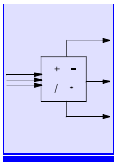

2.8 Stream Calculator

General Information

The Stream Calculator is a multi-purpose module intended to facilitate the manipulation of process streams in a PRO/II simulation flowsheet. There are two distinctly different modes of operation available: stream splitting and stream synthesis. A single Stream Calculator module may operate in either of these two modes exclusively, or may be configured to operate in both modes simultaneously. When configured to operate in both modes, a single set of feed streams and feed blending factors is utilized by both the splitting and synthesis calculations. However, each mode uses the feed streams and blending factors independently. In no way do the splitting calculations affect the synthesis calculations. In a completely complementary manner, the synthesis calculations never in any way affect the splitting calculations.

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PRO/II Note: Only selected topics are discussed here to clarify ambiguities and enhance user understanding of the purpose and use of the Stream Calculator module. Refer to Section 122, *Stream Calculator*, in the *PRO/II Keyword Input Manual* for information about all features and options available for this module.

Feed Blending Considerations

As stated in the *PRO/II Keyword Input Manual*, feed blending may be considered a third mode of operation, but this viewpoint is slightly misleading. In fact, feed blending is merely a preliminary setup operation that prepares available feed stream data for use in subsequent stream splitting and/or stream synthesis calculations. Without the subsequent splitting or synthesis calculations (which are required), feed blending performs no useful function.

Feed blending occurs whenever feed streams are present in the definition of a Stream Calculator module. The result of this blending is a single combined stream that is a composite of all the individually declared feed streams. The resultant combined feed then serves as the sole reference of feed stream data for all splitting and synthesis factors that refer to feed data. For splitting calculations, the **FOVHD** and **FBTMS** factors refer to the component compositions stored in the combined feed. For synthesis calculations, the **FPROD** factors refer to the component compositions stored in the combined feed.

The FEED statement allows the user to supply a single feed blending factor for each feed stream. Each such factor is a *relative scaling factor* that is used to multiply the total flowrate of its respective feed stream. All the feed streams then are blended together to yield the combined feed stream that has total rate dictated by the feed blending factors. The proportion of each component in the combined feed is the result of proportional blending based on the fraction of each component in the original individual feed streams.

It is important to remember that feed blending always occurs whenever two or more streams feed the Stream Calculator. All streams that do not have a feed blending factor supplied by the user assume a blending factor of unity. This means each such stream is blended at exactly 100% of its rate in the flowsheet.

The Stream Calculator allows the user to assign any value to each feed blending factor. A positive blending factor indicates additive blending of the stream while a negative factor causes subtracting a stream to create the combined feed. In this way, the careful user can create a combined feed of almost any desired composition.

Note that true mass balance between the Stream Calculator and the rest of the flowsheet is achieved only when all feed streams have a blending factor of unity. Blending factors greater than unity cause a virtual creation of mass flow while factors less than unity cause a virtual removal of mass. Note this ‘‘adjustment’’ represents a discontinuity between the mass contained in the individual feed streams and the single combined feed that is created. There is no accounting for this gain or loss, and any products of such a Stream Calculator that feed back into the flowsheet cause the flowsheet to be out of mass balance. However, whenever feed streams are present, mass balance is preserved across the Stream Calculator (i.e., the products and the combined feed are kept in mass balance).

Stream Splitting Considerations

The stream splitting capability of the Stream Calculator allows dividing the combined feed into two product streams of virtually any desired composition. This is a brute-force ‘‘black box’’ operation, since equilibrium and thermodynamic constraints (such as azeotrope formation) are **not** applied. This capability is useful when fast, non-rigorous modeling is desired or expedient. For example, assume a flowsheet under construction includes a rather complicated reactor. Further assuming the feed and desired product conditions are known, a Stream Calculator could be used as a quick, simple preliminary reactor model that would produce the desired reaction products without requiring the developer to worry about kinetics, reaction rates, and other reaction complexities. Development of the remainder of the flowsheet could proceed immediately while the time-consuming development of a rigorous reactor model could be deferred.

Stream splitting always requires the presence of at least one feed as well as both the **OVHD** (overhead) and **BTMS** (bottoms) product streams. All of the combined feed is distributed between these two products. If all feed streams have blending factor values of unity (i.e., 1.0), overall flowsheet material balance is preserved.

The stream splitting operation also requires the user to supply a splitting factor for every component in the flowsheet, even if that component does not appear in any of the feeds to the Stream Calculator. The disposition of each component must be defined in one and only one splitting factor specification. The most straightforward way to accomplish this is to define splitting factors for all components in terms of only one product. For example, use only **FOVHD**, **ROVHD**, and **XOVHD** splitting specifications to define all component splitting in terms of only the overhead product. The rate and composition of the bottoms stream then is calculated as the difference between the combined feed and the overhead product. Alternatively, use only **FBTMS**, **RBTMS**, and **XBTMS** splitting specifications to define all component splitting in terms of only the bottoms product. In the latter case, the rate and composition of the overhead product is calculated as the difference between the combined feed and the bottoms product. Splitting factors of zero exclude the component (or group of components) from the specified product stream. Negative splitting factor values are invalid.

Note: The **XOVHD** and **XBTMS** splitting factors specify only the relative composition of components in the overhead and bottoms products respectively. ***This means they do not and cannot be used as a basis for calculating the rate of either product***. Since mass balance between the combined feed and the products is always enforced, some splitting factor that establishes a basis for calculating product flowrates is required. For this reason, ***the distribution of at least one component must be specified using an FOVHD, FBTMS, ROVHD, or RBTMS separation factor.***

Stream Synthesis Considerations

Stream synthesis is useful for dynamically creating a stream or modifying the composition and rate of a stream during flowsheet convergence calculations. Stream synthesis does not require the presence of any feeds to the Stream Calculator, but always creates ‘‘something from nothing,’’ a virtual mass flow that introduces a discontinuity in the material balance of the flowsheet. Typically, the synthesized stream is intended to serve as an ‘‘source’’ stream that feeds the flowsheet. When used in this manner, the synthesized stream does not compromise the mass balance of the overall flowsheet since it is considered to originate in an ‘‘infinite source’’ that is external to the flowsheet.

Note: The **XPROD** splitting factors specify only the relative composition of components in the synthesized product. ***This means they do not and cannot be used as a basis for calculating the rate of the synthesized product***; some splitting factor that establishes an absolute basis for calculating product flow rate is required. For this reason, ***the rate of at least one component must be specified using an FPROD or RPROD separation factor.***

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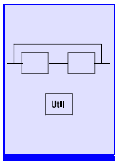
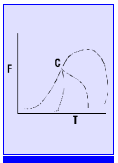


2.9 Utilities

This section describes a number of supplemental calculation methods available in PRO/II. These include the following calculations:

- Phase envelope
- Heating or cooling curve
- Binary vapor-liquid and vapor-liquid-liquid equilibria verification
- Hydrate prediction
- Exergy

These calculation modules are performed after the process flowsheet has solved, and therefore do not affect the flowsheet convergence.



2.9.1 *Phase Envelope*

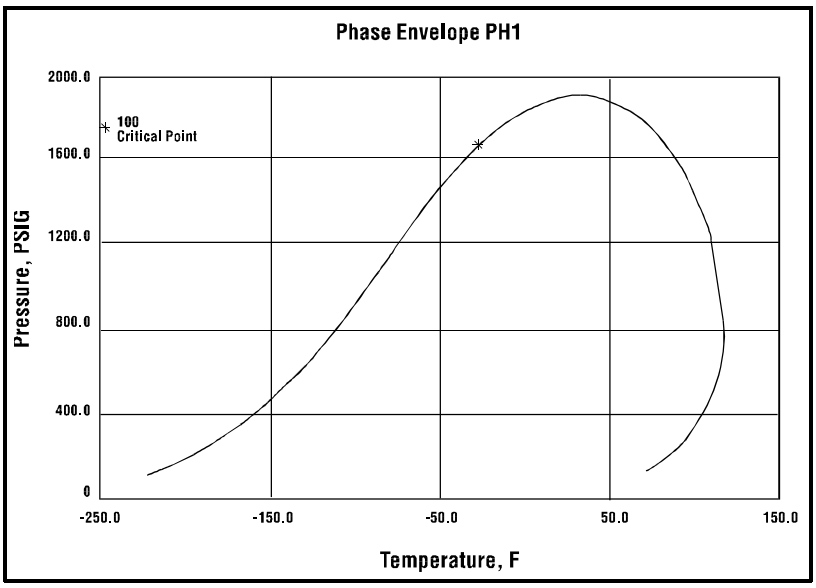
General Information

The PHASE ENVELOPE module generates a phase envelope or constant liquid fraction curve (in tablular or plot form) for streams using the Soave-Redlich-Kwong or Peng-Robinson equation of state methods.

Note: The phase envelope module is currently limited to the Soave-Redlich-Kwong and Peng-Robinson thermodynamic methods only.

Up to five separate curves or tables may be specified for each phase envelope module. Figure 2.9.1-1 shows a typical phase envelope:

Figure 2.9.1-1: Phase Envelope



Calculation Methods

Flash computations often fail at the critical conditions. However, for the Phase Envelope module, the true critical point, cricondentherm, cricondenbar, and points of the phase envelope are determined with the method of Michelsen. This method provides a direct solution for the mixture critical point, and encounters no difficulties in the critical region. Regions of retrograde condensation are also accurately predicted.

2.9.2

PRO/II Note: See the HCURVE section of this manual for more information on retrograde condensation.

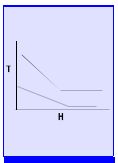
Michelsen developed his technique with the Soave-Redlich-Kwong method. However, the method may be applied to any equation of state provided that an algorithm for evaluation of component fugacities, and their first partial derivatives with respect to temperature, pressure, and composition for specified temperatures, pressures, compositions, and fluid states may be developed. We have extended his technique to include the Peng-Robinson equation of state.

Note: Water will always be treated as a regular component in PRO/II for phase envelope calculations, regardless of whether water is declared as a decanted phase or not.

Reference

Michelsen, M.L., 1980, Calculations of Phase Envelopes and Critical Points for Multicomponent Mixutres, *Fluid Phase Equil.*, **4**, pp. 1-10.

The Phase Envelope calculations are always performed after the flowsheet has fully converged, and therefore does not affect the convergence calculations. Also, like the HCURVE, this unit is not accessible via the CONTROLLER, MVC, or CASESTUDY.



2.9.2 Heating / Cooling Curves

General Information

The HCURVE module provides a variety of options to calculate and report properties of process streams in a PRO/II simulation. In general, a heating/cooling curve is generated for a process stream between two defined points or states: the user must provide information that defines both the initial point and end point of the process stream being investigated. The physical state of the stream must be fully defined at these two limiting points. The information presented here is intended to extend user understanding and provide insight into the capabilities and limitations of the HCURVE module. Several different types of curves may be requested, and each type of curve offers a number of options for defining the end-point states of the stream. Examples of data that sufficiently define a stream state include:

- Specifying both temperature and pressure, or
- Specifying enthalpy content and either temperature or pressure.

The stream itself always supplies all composition information.

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PRO/II Note: See Chapter 123, *Heating-Cooling Curves*, of the *PRO/II Keyword Input Manual* for input requirements and calculation options available for heating/cooling curves.

Calculation Options

Any number of heating / cooling curves may be requested in each HCURVE unit, but you must identify the process stream for each curve. Alternatively, instead of explicitly identifying a process stream, the HCURVE module allows you to specify a stream by describing a configuration of a unit operation such as a heat exchanger, flash drum, or distillation column. For example, you may elect to instruct the HCURVE module to generate a curve with points spaced at equal temperature and pressure increments between the inlet and outlet conditions on the hot side of a heat exchanger in the simulation. When using any of these options, the end-point states of the desired stream are obtained from the converged solution of the unit operation, and in general cannot be modified by supplying additional input data for the curve.

All calculations use the standard thermodynamic, flash, and transport techniques discussed in earlier sections of this manual and in the *PRO/II Keyword Input Manual* and *PROVISION User's Guide*. A single thermodynamic method set is used in each HCURVE module. When more than one thermodynamic method set is present in the simulation, a unit-specific method may be used to choose the *one* set that will be used for *all* curves in the HCURVE module. When the unit-specific method is not specified, the default thermodynamic data set will be used.

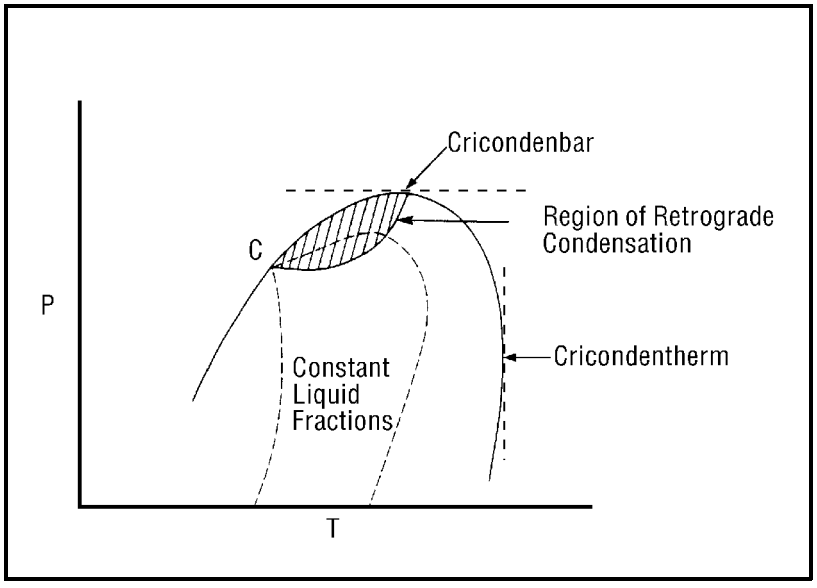
The **GAMMA** option available for most heating cooling curves is valid only when the thermodynamic method set being used employs a liquid activity K-value method.

Critical Point and Retrograde Region Calculations

The extreme phase discontinuities inherent at the critical point pose particularly severe calculation situations for dew and bubble curve generation, although all curve calculations experience some difficulties in this region. Generally, it is not uncommon for flash calculations to fail as the curve crosses the critical point. When possible, it is suggested that the Phase Envelope (see Section 2.9.1, *Phase Envelope* of this manual) module be used to generate a phase diagram, since that model can compute a complete phase diagram, including the critical point, and correctly finds both solutions when retrograde phenomena are present.

Many systems, commonly encountered in natural gas applications, exhibit a phase behavior known as ‘‘retrograde condensation.’’ That is, above the critical pressure in the two-phase region, it is possible for the condensate to vaporize as the temperature is **decreased.** For such systems, it often is possible to obtain two different **valid** solutions for the dew point temperature at a fixed pressure, depending on how the curves are initialized and the size of the temperature increments. Experience has shown that the Peng-Robinson (PR) K-value generator is somewhat more stable when predicting dew points in the retrograde region than is the Soave-Redlich-Kwong equation of state.

Figure 2.9.2-1: Phenomenon of Retrograde Condensation



VLE, VLLE, and Decant Considerations

The HCURVE module currently does not perform rigorous liquid-liquid equilibrium calculations. Systems exhibiting two liquid phases may be modeled only using ‘‘free water’’ thermodynamic method sets with the **DECANT=ON** option of the **WATER** statement activated (either explicitly or by default). In the HCURVE module, only a single liquid phase appears in the results produced by all rigorous VLLE K-value methods and VLE K-value methods that do no decant free water.

Water and Dry Basis Properties

HCURVE tables report several properties on a ‘‘DRY BASIS.’’ Dry basis is meaningful only when using a free-water decanting K-value method with the decant option activated (see *VLE, VLLE, and Decant Considerations* above). In this situation, dry basis means free water has been ignored during the calculation of the (dry) properties. This strategy applies only to liquid phase calculations; properties of vapor, even vapor containing water, are not affected. In the typical case, solubility and miscibility of water in the non-aqueous liquid phase are not considered when performing water decanting. This means, in almost all cases, that dry properties are calculated on a completely water-free basis that ignores all dissolved or entrained water as well as any ‘‘free’’ water. In a completely analogous manner, properties reported for the ‘‘WATER’’ liquid phase are only meaningful when a free-water decanting K-value method is used.

When using a non-decanting VLE K-value method, at most a single liquid phase is reported. When using a (non-decanting) rigorous VLLE K-value method, the HCURVE module ignores the liquid-liquid phase split and again handles all liquid as a single phase. In both of these cases, the (reported) single liquid phase always includes all of the liquid water that is present. This means that properties of the ‘‘decant’’ liquid are meaningless, and typically are reported as zero, missing, or ‘‘N/A’’ (i.e., not applicable).

GAMMA and KPRINT Options

The **PROPERTY** statement allows the user to stipulate sets of properties that will be reported for every heating/cooling curve generated in an HCURVE module. The **GAMMA** and **KPRINT** options allow the user to request property reports for individual heating cooling curves. The **GAMMA** option is a superset of the **KVALUE** option; that is, **GAMMA** prints all the same information as the **KVALUE** option and adds more data to the report. For this reason, there is no benefit to including both options for a single heating/cooling curve.

Both GAMMA and KVALUE generate a report for each component in the stream at each point of the heating/cooling curve. Table 2.9.2-1 summarizes the information reported at each point.

Table 2.9.2-1: GAMMA and KPRINT Report Information

Property	GAMMA	KPRINT
Point ID number	X	X
Temperature	X	X
Pressure	X	X
Component name	X	X
Component composition in vapor	X	X
Component composition in liquid	X	X
Component equilibrium K-value	X	X
Component name	X	
Component gamma (activity coefficient)	X	
Component vapor pressure	X	
Pure component fugacity coefficient	X	
Component Poynting correction	X	
Component vapor fugacity coefficient	X	

Availability of Results

Heating/Cooling units always perform their calculations during the output pass of the flowsheet convergence module whenever PRO/II executes. This means that HCURVE modules are not considered until after the completion of all calculations needed to solve the flowsheet. For this reason, the following applies to data generated by HCURVE units:

- HCURVE data are not available to CONTROLLERs or OPTIMIZERs to control or modify flowsheet calculations,
- HCURVE data are not accessible through the SPECIFICATION feature
- HCURVE data cannot be used to affect flowsheet convergence calculations.

However, HCURVE results are stored in the problem database files and appear in the standard output reports of the simulation. In addition, HCURVE results may be retrieved through facilities of the PRO/II Data Transfer System (PDTS) for use in user-written applications (see the *PRO/II Data Transfer System User's Guide*). Also, a small subset of the HCURVE data is included in the export file created by using the DBASE option.

5

PRO/II Note: See Chapter 5, *General Data*, in the *PRO/II Keyword Input Manual* for more information on the DBASE option.

The **DBASE DATA=PC1** option creates an ASCII database file that includes selected data for each heating/cooling curve generated by every HCURVE unit in the problem flowsheet. A typical example of the HCURVE data included in the **.ASC** file is shown in Table 2.9.2-2.

Table 2.9.2-1: Sample HCURVE .ASC File

```
 13 F100    0    0    12
 228.00      1000.00       281.89       108.45      0.00000E+00   390.34
 21.325       4.7685      0.00000E+00  0.81725      0.18275      0.00000E+00
 232.00      1000.00       220.65       227.53      0.00000E+00   448.18
 16.231       9.8631      0.00000E+00  0.62201      0.37799      0.00000E+00
 236.00      1000.00       162.69       339.24      0.00000E+00   501.93
 11.598       14.496      0.00000E+00  0.44446      0.55554      0.00000E+00
 240.00      1000.00       115.57       430.33      0.00000E+00   545.90
 7.9673       18.126      0.00000E+00  0.30533      0.69467      0.00000E+00
 244.00      1000.00        79.685       500.58      0.00000E+00   580.26
 5.3071       20.787      0.00000E+00  0.20339      0.79661      0.00000E+00
 248.00      1000.00        52.146       555.42      0.00000E+00   607.57
 3.3549       22.739      0.00000E+00  0.12857      0.87143      0.00000E+00
 252.00      1000.00        30.150       600.03      0.00000E+00   630.18
 1.8744       24.219      0.00000E+00  0.71833E 01  0.92817      0.00000E+00
 256.00      1000.00        11.608       638.20      0.00000E+00   649.81
0.69776       25.396      0.00000E+00  0.26741E 01  0.97326      0.00000E+00
 258.77      1000.00      0.00000E+00    662.26      0.00000E+00   662.26
0.00000E+00   26.094      0.00000E+00  0.00000E+00   1.0000       0.00000E+00
 260.00      1000.00      0.00000E+00    664.14      0.00000E+00   664.14
0.00000E+00   26.094      0.00000E+00  0.00000E+00   1.0000       0.00000E+00
```

This data in the table above should be interpreted as follows:

@DBHCRV HC00 ISO 13 F100 0 0 12

The statement above identifies the data as an isothermal (**ISO**) heating/cooling curve generated by HCURVE unit **HC00** for stream **F100**. The remaining entries on this line are included for use by PRO/II utility functions such as IMPORT, and are not described here.

The subsequent lines of information in Table 2.9.2-2 present a limited subset of data generated for this stream by the HCURVE calculations. Each point of the curve is summarized on two lines of the listing. Table 2.9.2-3 interprets the data for a typical point of the curve.

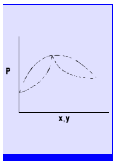
Table 2.9.2-3: Data For an HCURVE Point

```
                          ---------------  Enthalpy,  K*Kcal/h ------------------
 Temp C      Pres mmHg     liquid       vapor     water (decant)      total
 228.00        1000.00     281.89       108.45      0.00000E+00      390.34

---------  mole rate, Kg mole/hr -------      ------------  Mole Fraction (wet) ----------
  liquid   vapor    water (decant)       liquid        vapor    water (decant)
  21.325   4.7685      0.00000E+00       0.81725       0.18275      0.00000E+00
```

All the data are expressed in the dimensional units used to supply input data in the original problem definition. For example, Table 2.9.2-3 indicates temperature is presented in degrees Celsius. Alternitively, if the dimensional unit of temperature in the original input file had been, for example, Rankine, then the temperatures presented in Tables 2.9.2-2 and 2.9.2-3 would represent Rankine temperatures. This reasoning also applies to the enthalpy and rate data.

Note: The information available in the **.ASC** file always is limited to the data shown in Table 2.9.2-3, *regardless of the type of heating/cooling curve or the printout options included in the HCURVE unit.*



2.9.3 Binary VLE/VLLE Data

General Information

The Binary VLE/VLLE Data module (BVLE) may be used to validate binary vapor-liquid or vapor-liquid-liquid equilibrium data for any given pair of components. This unit operation generates tables and plots of K-values and fugacity coefficients versus liquid and vapor composition at a specified temperature or pressure. A number of plot options are available.

Any thermodynamic VLE or VLLE K-value method may be used to validate the VLE or VLLE data. For liquid activity thermodynamic methods, the following are calculated by the BVLE module:

- K-values
- Liquid activity coefficients
- Vapor fugacity coefficients
- Vapor pressures
- Poynting correction.

For non-liquid activity methods such as the SRK cubic equation of state, the following are calculated by the BVLE module:

- K-values
- Liquid fugacity coefficients
- Vapor fugacity coefficients.

Only selected input and output features of the Binary VLE / VLLE Data module are discussed in this reference manual.

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PRO/II Note: See Chapter 126, *Binary VLE/VLLE Data*, of the *PRO/II Keyword Input Manual* for information on all features and options available for this module.

The BVLE unit operation does not affect flowsheet convergence. It is always executed during the output calculations phase of simulator execution, after the flowsheet has fully converged, and therefore does not affect the convergence calculations. Also, like the HCURVE, this unit is not accessible via the CONTROLLER, MVC, or CASESTUDY.

Input Considerations

One feature worth discussing further is the **XVALUE** option of the **EVALUATE** statement. Quite often, tables of generated data bracket, but do not exactly match, points of great interest such as experimental compositions. The **XVALUE** option allows the user to specify exact component mole fraction values so these points can be very closely investigated.

The **XVALUE** entry accepts liquid/vapor mole fractions for component *i*, one of the two components declared on the **COMP** entry (on the same **EVAL** statement). If only one value is given, it is assumed to be the starting value, with the number of points determined by the **DELX** and **POINTS** entries. If two values are given, they are assumed to be the starting and terminal values, with the number of points to generate specified by the **POINTS** entries. The default starting and ending (mole fraction) values are 0.0 and 1.0. When three or more points are supplied, only those specific points are generated.

Output Considerations

Results of each **EVALUATE** statement are printed as tables or optional plots. The format of the report tables changes depending upon whether the thermodynamic methods set that is being used is able to predict two liquid phases (VLLE) or only a single liquid phase (VLE). The tables of results are clearly labeled and only two additional notes are presented here:

1. In the mole fraction results tables, X(1) in the header represents the molar liquid fraction and Y(1) represents the molar vapor fraction of component one. X(2) and Y(2) identify the same quantities for the second component of the binary. In VLLE results listings only, the first and second liquid phase columns are distinguished by asterisks. For example, X(1)* represents mole fractions of component 1 in the first liquid phase while X(1)** is used for fractions of component 1 in the second liquid phase. Since at most only a single vapor phase exists, asterisks never appear with vapor data headings (such as Y(1) or Y(2)).
2. In VLLE results listings of activity coefficients and vapor fugacity coefficients, an additional column appears labeled *Distribution Coefficient*. The distribution coefficients are liquid-liquid equilibrium analogs of vapor-liquid equilibrium K-values. Therefore, the distribution coefficient of component *i* would be defined as:

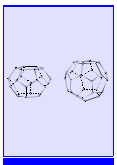
$$K_{Di} = x_i^I / x_i^{II} \qquad (1)$$

where:

K_{DI} = liquid-liquid distribution coefficient of component *i*

x_i = liquid mole fraction of component *i*

I, II represent the first and second liquid phases, respectively



2.9.4 Hydrates

General Information

PRO/II contains calculation methods to predict the occurrence of hydrates in mixtures of water and hydrocarbons or other small compounds. PRO/II can identify the temperature/pressure conditions under which the hydrate will form, as well as identify the type of hydrate that will form (type I or type II). The effect of adding an inhibitor (either methanol, sodium chloride, ethylene glycol, di-ethylene glycol, or tri-ethylene glycol) on hydrate formation can also be predicted by PRO/II.

Theory

Hydrates are formed when water acts as a ‘‘host’’ solid lattice to ‘‘guest’’ molecules which occupy a certain portion of the lattice cavity. Only molecules which are small in size, and of a certain geometry may occupy these guest cavities. These hydrates are a form of an inclusion compound known as clathrates, and no chemical bonds form between the water lattice and enclosed gas molecules. Two different types of hydrates can be identified. Their characteristics are given in Table 2.9.4-1. Table 2.9.4-2 lists the gas molecules which may occupy the cavities of these hydrates.

Note: Water does not have to be specifically defined by the user as a component in the system for hydrate calculations to proceed. PRO/II will assume the presence of free water when hydrate calculations are requested.

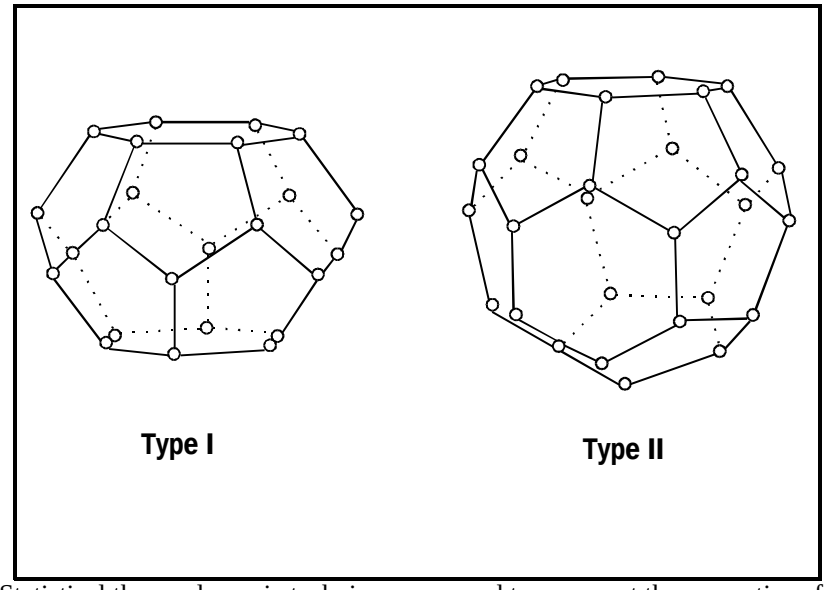
Table 2.9.4-1: Properties of Hydrate Types I and II

Property	Type I	Type II
Number of water molecules per unit cell	46	136
Number of small cavities per cell	2	16
Number of large cavities per cell	6	8
Cavity diameter (Å)		
Small	7.95	7.82
Large	8.60	9.46

Table 2.9.4-2: Hydrate-forming Gases		
Methane	Ethane	Propane
N-butane	Isobutane	Carbon dioxide
Hydrogen sulfide	Nitrogen	Ethylene
Propylene	Argon	Krypton
Xenon	Cyclopropane	Sulfur hexafluoride

The hydrates formed are stabilized by forces between the host water and guest gas molecules.

Figure 2.9.4-1: Unit Cell of Hydrate Types I and II



Statistical thermodynamic techniques are used to represent the properties of these hydrates. At equilibrium, the chemical potential of the water in the hydrate phase is equal to the chemical potential of water in any other phase present (e.g., gaseous, ice, or liquid). In 1958, van der Waals and Platteeuw derived the following equation relating the chemical potential of water in the hydrates to the lattice molecular parameters:

$$\Delta \mu_w^H = RT \sum_i \upsilon_i h \left(1 - \sum_k Y_{ki}\right) \qquad (1)$$

$$i = 1,2, ..., N_{cav}$$

$$k = 1,2, ..., N_{comp}$$

where:

$\Delta \mu_w^H$ = difference in chemical potential between the filled gas-hydrate lattice and the empty hydrate lattice

v_i = number of cavities of type i in the hydrate

Y_{ki} = probability of cavity i being occupied by a hydrate-forming molecule of type k

The probability, Y_{ki}, may be described by a Langmuir-type adsorption expression:

$$Y_{ki} = \frac{C_{ki} f_k}{1 + \sum_j C_{ji} f_j} \qquad (2)$$

$$j = 1,2, ..., N_{comp}$$

$$k = 1,2, ..., N_{comp}$$

where:

f_k = fugacity of hydrate-forming component k

C_{ki} = adsorption constant

Using equation (2), equation (1) then becomes:

$$\Delta \mu_w^H = RF \sum_i \upsilon_i h \left(1 + \sum_k C_{ki} f_i\right) \qquad (3)$$

The adsorption constant C_{ki} is related to the spherical-core cell potential by:

$$C_{ki} = \frac{1}{kT} \int_0^\infty \exp\left(-\frac{W(r)}{kT}\right) 4\pi r^2 \, dr \qquad (4)$$

where:

k = Boltmann's constant = 1.38 x 10^{-16} erg/K

T = temperature, K

$W(r)$ = spherical cell potential, erg

r =

radial coordinate, (Å)

The spherical cell potential, W, is a function of the radius of the unit cell, the coordination number of the cavity containing the gas molecule, and sum of the interactions between the enclosed gas molecule and the water molecules in the lattice wall.

The Kihara potential between a single gas molecule and one water molecule in the lattice wall is given by:

$$\Gamma(r) = 4\varepsilon\left[\left(\frac{\sigma}{r-2\alpha}\right)^{12} - \left(\frac{\sigma}{r-2\alpha}\right)^{6}\right] \text{ for } r > 2\alpha \quad (5a)$$

$$\Gamma(r) = \infty \text{ for } r \le 2\alpha \quad (5b)$$

where:

Γ = Kihara potential, ergs

ε = characteristic energy, ergs

α =

core radius, (Å)

$\sigma + 2\alpha$ =

collision diameter, (Å)

Summing the gas-water interactions over the entire lattice yields:

$$W(r) = 2\varepsilon z\left[\frac{\sigma^{12}}{R_c^{11} r}\left(\delta^{10} + \frac{\alpha}{R_c}\delta^{11}\right) - \frac{\sigma^{6}}{R_c^{5} r}\left(\delta^{4} + \frac{\alpha}{R_c}\delta^{5}\right)\right] \quad (6)$$

and,

$$\delta^N = \left[\left(1 - \frac{r}{R_c} - \frac{\alpha}{R_c}\right)^{-N} - \left(1 + \frac{r}{R_c} - \frac{\alpha}{R_c}\right)^{-N}\right] / N, \text{N} = 4, 5, 10, 11 \quad (7)$$

where:

z = coordination number of cavity

R_c = cell radius

When liquid water is present with the hydrate, the chemical potential difference between water in the liquid phase and the empty hydrate is given by:

$$\Delta\mu_w^L = RT\sum_i \upsilon_i \, h\left(1 + \sum_k C_{ki} f_k\right) + RT\, h\, x_w \quad (8)$$

where:

$\Delta\mu_w^L$ = chemical potential difference between water in the liquid phase and the empty hydrate

x_w = mole fraction of water in the liquid phase

For gas mixtures, a binary interaction parameter, a_j, representing the interaction between the most volatile hydrate-forming gas molecule and all other molecules is introduced into equation (8).

(9)

$$\Delta\mu_w^L = RT$$

$$\left[\prod k\left\{1 + 3(\alpha_k - 1)y_k^2 - 2(\alpha_k - 1)y_k^3\right\}\right]\left[\sum_i \upsilon_i \, h\left(1 + \sum_k C_{ki} f_k\right) + RTh\, x_w\right]$$

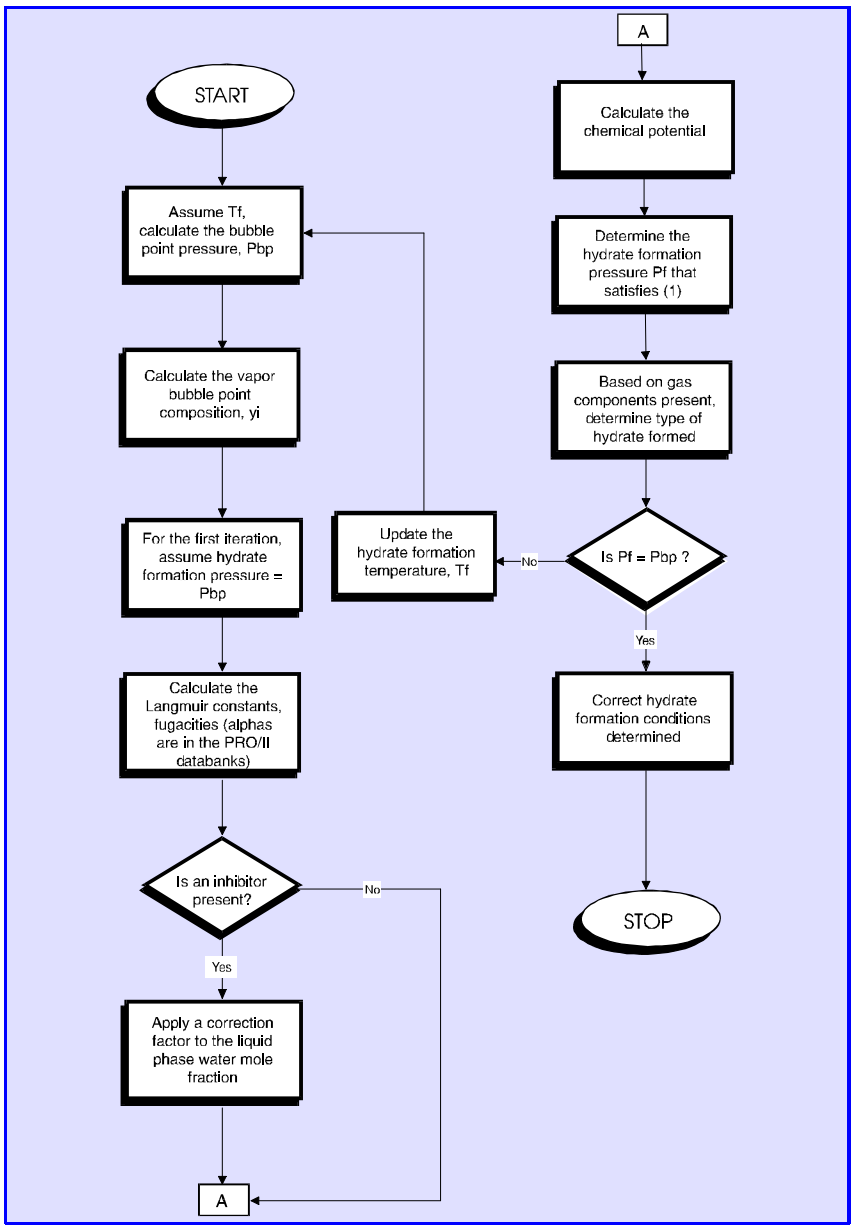
where:

α_k = binary interaction parameter between the most volatile component and component k

y_k = mole fraction of component k in the vapor phase

The method used for determining the temperature and pressure conditions under which hydrates form is given in Figure 2.9.4-2.

Figure 2.9.4-2: Method Used to Determine Hydrate-forming Conditions


START
Assume Tf, calculate the bubble point pressure, Pbp
Calculate the vapor bubble point composition, yi
For the first iteration, assume hydrate formation pressure = Pbp
Calculate the Langmuir constants, fugacities (alphas are in the PRO/II databanks)
Is an inhibitor present?
No
Yes
Apply a correction factor to the liquid phase water mole fraction
A
A
Calculate the chemical potential
Determine the hydrate formation pressure Pf that satisfies (1)
Based on gas components present, determine type of hydrate formed
Is Pf = Pbp ?
No
Update the hydrate formation temperature, Tf
Yes
Correct hydrate formation conditions determined
STOP

References

1. Munck, J., Skjold-Jorgensen, S., and Rasmussen, P., 1988, Computations of the Formation of Gas Hydrates, *Chem. Eng. Sci.*, **43**(10), pp. 2661-2672.
2. Ng, H.-J., and Robinson, D.B., 1976, The Measurement and Prediction of Hydrate Formation in Liquid Hydrocarbon-Water Systems, *Ind. Eng. Chem. Fundam*., **15**(4), pp. 293-298.
3. Parrish, W. R., and Prausnitz, J.M., 1972, Dissociation Pressures of Gas Hydrates Formed by Gas Mixtures, *Ind., Eng., Chem. Proc., Des. Develop.*, **11**(1), pp. 26-35.
4. Peng, D. Y., and Robinson, D.B., 1979, Calculation of Three-Phase Solid-Liquid-Vapor Equilibrium Using an Equation of State, *Equations of State in Engineering and Research, Advances in Chemistry Series, No. 182, ACS*, pp. 185-195.

$B = H\text{-}TS$

2.9.5 Exergy

General Information

Exergy (or availability) calculations may be requested by the user by supplying the EXERGY statement in the General Data Category of input. All entries are optional. When requested, exergy calculations are performed in the final stages of writing the PRO/II output report. As such, exergy calculations are not available during, and in no way whatsoever affect, flowsheet convergence. Exergy results appear after the Stream Summary reports in the PRO/II output report.

The availability function, B, is defined as:

$$B = H - TS \qquad (1)$$

where:

H = enthalpy
T = temperature
S = entropy

Interpreting Exergy Reports

In the exergy report, enthalpy and entropy are reported on a total stream basis and reflect the actual state of the stream (i.e., at whatever phase conditions prevail at the actual stream temperature and pressure).

The availability functions shown in Table 2.9.5-1 are provided in the exergy report:

Table 2.9.5-1: Availability Functions

Availability Function	Description
B(EXS)	The exergy (availability) at the EXisting State (i.e., actual state) of the stream.
B(TES)	The exergy (availability) at reference temperature Tzero and actual stream pressure.
B(EVS)	The exergy (availability) at the EnVironmental State (i.e., the reference or "zero" state at Tzero and Pzero). B(EVS) TOTAL is calculated rigorously assuming the stream is actually at Tzero, Pzero conditions, and no assumptions are made about the phase state. B(EVS) VAPOR also is calculated at Tzero and Pzero, but an *a priori* assumption is made that the stream is exclusively in a vapor state. This is provided as a convenience to users who make this simplifying assumption when performing manual calculations.
B(MES)	This represents stream exergy (availability) at Modified Environmental State, computed as follows: $B(MES) = H - Tzero * \Sigma (S_i + (x_i * log(x_i)))$ where: H = total stream enthalpy S_i = entropy of component i x_i = mole fraction of component i in the stream These calculations are carried out at the same conditions used to compute B(EVS) VAPOR.
E(T)	This function is equal to B(EXS) - B(TES)
E(P)	This function is equal to B(EXS) - B(EVS) VAPOR
E(M)	This function is equal to B(EXS) - B(MES)

For unit operations, the availability is calculated as follows:

$$DELTA{-}B = \Sigma\, B(EXS) feeds - \Sigma\, B(EXS)\ products\ (W{-}EXT) \qquad (2)$$

The external work done by the unit operation and the heat duty of the unit operation are also given in the exergy report.

References

1. Venkatesh, C.K., Colbert, R.W., and Wang, Y.L., Exergy Analysis Using a Process Simulation Program, presented at National Converence of the Mexican institute of Chemical Engineers, October 17, 1980.
2. de Nevers, Noel, and Seader, J.D., Mechanical Lost Work, Thermodynamic Lost Work, and Thermodynamic Efficiencies of Processes, presented at 86th AIChE National Meeting, Houston, Texas, April 1979.

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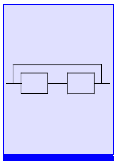


2.10 Flowsheet Solution Algorithms

PRO/II is able to find all recycle streams of a flowsheet and generate a unit calculation sequence. For loop convergence, direct substitution as well as Wegstein and Broyden acceleration are available.

2.10.1 Sequential Modular Solution Technique

General Information

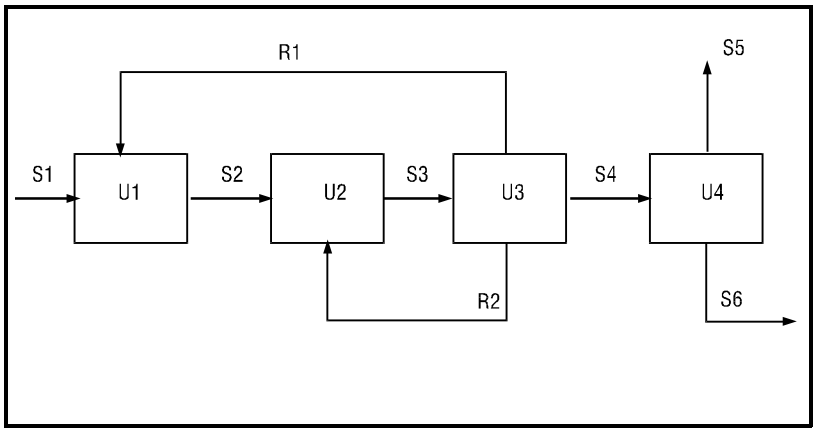
PRO/II solves process flowsheets using a *Sequential Modular Solution Technique*. This technique solves each individual process unit, applying the best solution algorithms available. Additionally, PRO/II applies several advanced techniques known as *Simultaneous Modular Techniques*, to enhance simulation efficiency.

Methodology

Any given simulation is equivalent to a large system of nonlinear simultaneous equations. This system of equations includes the evaluation of all necessary thermodynamic properties for all streams in the flowsheet, as well as all rates and compositions using the selected thermodynamic and unit models. In principle, it is possible to solve all these equations simultaneously, but PRO/II utilizes a different approach: *Every unit in the flowsheet is solved using the most efficient algorithms developed for each case*. For example, one can choose different methods for multiple distillation columns, ranging from shortcut to a variety of rigorous models and, for each case, PRO/II will use the corresponding specialized column algorithms. Should an error occur in any unit, due, for example, to incorrect column initialization or poorly chosen design parameters, it can be easily identified, confined and corrected.

To calculate a flowsheet of interconnected units, a sequence of unit calculations is determined automatically (or optionally provided by the user). If recycles are present, an iterative scheme is set up where recycle streams are ‘‘torn’’ and a succession of convergent ‘‘guesses’’ is created. These guesses are obtained by directly substituting the values calculated in the previous pass through the flowsheet (the Direct Substitution technique) or by applying special recycle acceleration techniques (see Section 2.10.3, *Acceleration Techniques*). For example, consider the following schematic flowsheet:

Figure 2.10.1-1: Flowsheet with Recycle



One possible solution sequence for this flowsheet is U1, U2,U3,U4,U5. In this sequence there are two recycle streams, R1 and R2. The subsequence U2,U3,U4 is a recycle loop and is solved repeatedly until convergence of the recycle streams is achieved.

Note: The Sequential Modular Solution Technique provides physically meaningful solution strategies, therefore allowing a process simulation to be easily constructed, debugged, analyzed, and interpreted.

Recently, the *Simultaneous Modular Solution* concept has been coined for *the art of flexibly solving simulation problems made up of process modules, introducing some aspects of equation-oriented strategies.* This new concept covers several techniques to improve the performance of strictly sequential modular solvers, including:

- Optimal tear streams selection
- Controlled simulations
- Unit grouping
- Stream referencing
- Flowsheet specifications
- All stream/tear stream convergence
- Linear and nonlinear derived models
- Inside-out strategies
- Simple-rigorous iterative procedures (two-tier algorithms).

PRO/II applies several simultaneous modular techniques when solving process flowsheets. Overviews of optimal tear stream techniques can be found in section 2.10.2, *Calculation Sequence and Convergence*, and the use of Controllers in simulations is reviewed in section 2.10.4, *Flowsheet Control*. Several other strategies (inside-out, all stream convergence, Simple-rigorous) are used to solve individual models.

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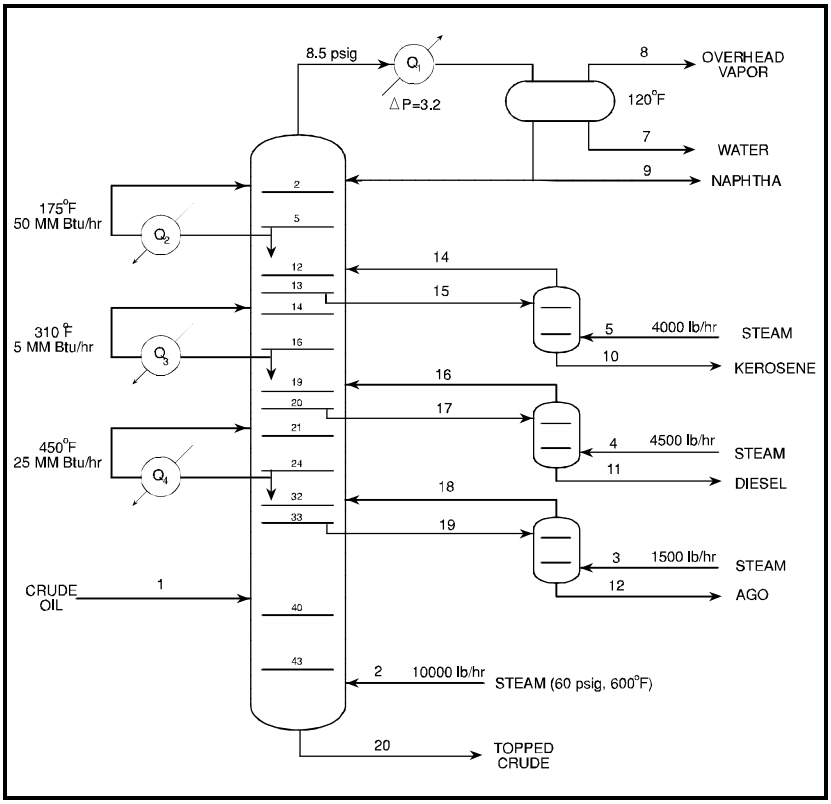
PRO/II Note: Stream referencing, which is very useful in enhancing convergence properties of recycles involving only heat exchangers (thermal recycles) is described in Chapter 33, *Reference Streams*, of the *PRO/II Keyword Input Manual*. See Chapter 44, *Specs, Constraints, and Objectives*, for information on flowsheet specifications.

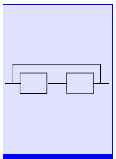
Process Unit Grouping

PRO/II uses *Unit Grouping* to allow improved simulation efficiency. Unit grouping is a special technique that simultaneously solves groups of units that are closely associated. One example of this is the integration of sidestrippers and pumparounds with column units. Consider the crude column shown in Figure 2.10.1-2:

Figure 2.10.1-2: Column with Sidestrippers



There are three pumparounds and three sidestrippers in the flowsheet. A strict application of the Sequential Modular Solution Technique requires six tear streams. Instead, by grouping the column and sidestrippers and solving them simultaneously, the number of tear streams is reduced to only three pumparound recycles. Moreover, if the attached heat exchangers corresponding to the pumparounds are also grouped, a unique model is obtained that does not contain recycles, further improving the simulation efficiency.



2.10.2 Calculation Sequence and Convergence

General Information

PRO/II performs an analysis of the flowsheet and determines the recycle streams and the loops of units with which they are associated. Then, tear streams and a solving sequence are determined. The user can override all these calculations and define his/her own calculation sequence. Initial estimates for the tear streams are desirable but not mandatory. If good estimates are provided, convergence will be achieved faster.

Tearing Algorithms

Two calculation sequence methods are available:

Minimum Tear Streams (SimSci Method)

This default sequencing method uses improved algorithms developed by SimSci to determine the best sequence for calculation purposes. This method provides a calculation sequence featuring a minimum number of tear streams.

Alternate Method (Process Method)

This method determines the sequence based partially on the order in which the unit operations were placed during the construction of the flowsheet. The units which were placed first are likely to be solved earlier than the units which were placed at a later time.

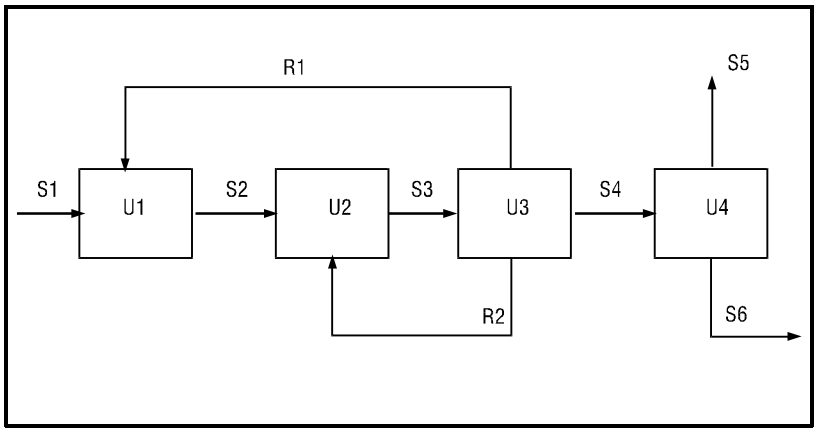
Both methods determine the independent calculation loops in the flowsheet, moving all calculations not affected by the recycle streams outside these independent loops. These units will not be calculated until the loops are solved. Then, for each loop, a tear set is determined. In the case of the *SimSci Method*, a minimum tear set based on the algorithm developed by Motard and Westerberg (1979) is used. If more than one choice is available for the tear set, the *Simsci Method* will pick the stream that has been initialized by the user. In the case of the *Process Method*, an algorithm that preserves as much as possible the order in which the user placed the units is used.

Single variable controllers which affect units within loops *will be* included in the loops. In turn, multivariable controllers and optimizers which affect units within loops *will not* be included in the loops. If any of these options is not desired a user-defined calculation sequence should be used.

Recycle loops concern two primary effects: *Composition* and *Thermal* changes for streams. The reference stream concept in PRO/II may often be used to redefine the tearing process and eliminate thermal recycles.

To illustrate how both algorithms find tear sets and calculation sequences, consider the following simplified flowsheet shown in Figure 2.10.2-1.

Figure 2.10.2-1: Flow-sheet with Recycle



Given the way this flowsheet is drawn, it has two recycle streams (R1,R2). The *SimSci method* will find the calculation sequence U3,U1,U2,U4 as only one tear stream (S3) and is the minimum tear set. The sequence U3,U1,U2, will be solved until convergence is reached and only then, unit U4 will be solved. Depending of the sequence entered by the user, the *Process Method* will identify the calculation sequences shown in Table 2.10.2-1.

Table 2.10.2-1: Possible Calculation Sequences

Order of Units Entered by the User	Calculation Sequence	Tear Streams
a) U1,U2,U3,U4	U1,U2,U3,U4	R1,R2
b) U1,U3,U2,U4	U1,U3,U2,U4	R1,S3
c) U2,U1,U3,U4	U2,U1,U3,U4	S2,R2,R1
d) U2,U3,U1,U4	U2,U3,U1,U4	S2,R2
e) U3,U1,U2,U4	U3,U1,U2,U4	S3
f) U3,U2,U1,U4	U3,U2,U1,U4	S3,S2
g) U4,U3,U2,U1	U3,U2,U1,U4	S3,S2
h) U3,U4,U2,U1	U3,U2,U1,U4	S3,S2

Note: The *Process Method* always preserves the user input sequence of units of a loop (U1,U2,U3 in this case), picking the tear streams accordingly, and placing units not belonging to loops before or after them as needed (see cases g and h in Table 2.10.2-1).

Reference

Motard, R.L. and Westerberg, A.W., 1979, DRC-06-7-79.

Convergence Criteria

Convergence is defined as being met when the following three requirements are achieved for two successive determinations of the recycle streams:

Component flow convergence test:

$$\left(\begin{matrix}Error\ in\ flow\ of\\ component\ i\end{matrix}\right) = \left|\frac{m_i^{n-1} - m_i^n}{m_i^n}\right| \le e_c = \left(\begin{matrix}Component\\ flow\ tolerance\end{matrix}\right) \quad (1)$$

where:

m_i^n and m_i^{n-1} = current and last values of the flow of component *i* in the recycle streams

Only components with mole fractions greater than a threshold value (default is 0.01) are considered for the above test. The component tolerance and threshold value may be set by the user using the TOLERANCE statement in the General Data category of input. Values of these tolerances may also be provided on the LOOP statements. Care should be exercised that inside loop tolerances are set always as tight or tighter than those for outside loops.

Temperature convergence test:

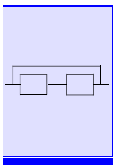
$$\left(\begin{matrix}Error\ in\\ temperature\end{matrix}\right) = \left|T_n - T_{n-1}\right| \le e_T = \left(\begin{matrix}Temperature\\ tolerance\end{matrix}\right) \quad (2)$$

Pressure convergence test:

$$\left(\begin{matrix}Error\ in\\ pressure\end{matrix}\right) = \left|\frac{P_n - P_{n-i}}{P_n}\right| \le e_p = \left(\begin{matrix}Pressure\\ tolerance\end{matrix}\right) \quad (3)$$

Default component flow, temperature and pressure tolerances of e_c = 0.01, e_T = 1.0°F (0.55°C) and e_p = 0.01 will be assigned by PRO/II. These tolerances may also be redefined in the General Data category of input or on the LOOP statement.

These convergence tests are applied to all streams, but the user has the option to apply them to the tear streams only.



2.10.3 Acceleration Techniques

General Information

Unless acceleration techniques are requested by the user, PRO/II will use direct substitution for closure of all recycle streams. This method usually works well; however, for loops in which closure is asymptotic an acceleration technique becomes desirable to reduce the number of trials required.

Wegstein Acceleration

The Wegstein acceleration technique takes advantage of the result of the previous trials, but ignores the interaction between different components. To use this technique, at least one trial must be made with direct replacement. Let $\bar{x}_k$ represent the estimated rate of a component or a temperature of a recycle stream at the beginning of trial k and x_{k+1} the calculated rate or temperature after trial k. The estimated rate for trial $k + 1$, $\bar{x}_{k+1}$, will be computed using these values as follows:

$$\bar{x}_{k+1} = q\bar{x}_k + (1-q)x_{k+1} \qquad (1)$$

In equation (1), q is the so-called acceleration factor and is determined by the following formula

$$q = \frac{w}{w-1} \qquad (2)$$

where:

$$w = \frac{x_{k+1} - x_k}{\bar{x}_k - \bar{x}_{k-1}} \qquad (3)$$

Table 2.10.3-1 shows how values of q affect convergence.

Table 2.10.3-1: Significance of Values of the Acceleration Factor, q

q	Convergence Region
q<0	Acceleration
q=0	Direct Substitution
0<q<1	Damping
q=1	Total damping (no convergence)

The more negative the value of q, the faster the acceleration. However, if the value of q thus determined is used without restraint, oscillation or divergence often results. It is therefore always necessary to set upper and lower limits on the value of q. These limits should be set based on the stability of the recycle stream. Normally, the upper limit should be at 0.0. A conservative value for the lower limit may be set at, -20.0 or -50.0 to speed up the convergence.

The Wegstein acceleration can be applied only after one or more trials with direct replacement have been made. If the initial estimate of the recycle stream composition is far different from the expected solution, e.g., zero total rate, a number of trials should first be made with direct replacement. Once started, Wegstein acceleration may be applied every trial or at frequencies specified by the user.

Recommended Uses for Wegstein

The Wegstein method works best for situations in which convergence is unidirectional; that is when a key component (or components) either builds up or decreases in a recycle stream. Because the Wegstein method does not consider the interaction effects of components, it may not be suitable for cases involving multiple recycle steams which are interdependent. Under these conditions the method may cause oscillation and hinder convergence. If oscillation occurs with direct replacement, upper and lower *q* values at 0.5 may be used in the Wegstein equation, forcing averaging to take place.

Reference

Wegstein, J. H., 1958, *Comm. ACM*, 1, No. 6, 9.

Broyden Acceleration

Broyden's method is a Quasi-Newton method. It consists of updating the inverse of the Jacobian at each iteration instead of calculating it or approximating it numerically. This method takes specifically into account all interactions between component rates and temperature of all streams included in the recycle loop. Let $\bar{x}_k$ represent the estimated rate of all components in a recycle stream at the beginning of trial k and x_{k+1} the calculated rate after trial k. Broyden uses an approximation ($-H_k$) to the inverse of the Jacobian which is being updated at every iteration. Broyden's procedure provides $\bar{x}_{k+1}$ as follows:

$$\bar{x}_{k+1} = \bar{x}_k + d_k \Delta x_k \qquad (4)$$

where:

d_k = a damping factor

In equation (4), Δx_k is given by:

$$\Delta x_k = H_k (x_{k+1} - \bar{x}_k) \qquad (5)$$

The update of H_k is performed using the following formula:

$$H_k = H_{k-1} - \frac{(H_{k-1}\, y_k + d_k\, \Delta x_{k-1})\, \Delta x_{k-1}^T\, H_{k-1}}{\Delta x_{k-1}^T\, H_{k-1}\, y_k} \quad (6)$$

where:

$$y_k = (x_{k+1} - \bar{x}_k) - (x_k - \bar{x}_{k-1}) \quad (7)$$

The algorithm starts with $H_0 = I$, avoiding thus expensive numerical calculations and inversion of the Jacobian. The damping factor has a default value d_k=1 at every iteration, and it is reset to a smaller value automatically to prevent the new estimates $\bar{x}_{k+1}$ from becoming negative.

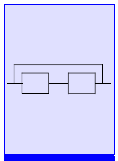
Recommended Uses for Broyden

It is recommended that the Broyden acceleration be applied only after sufficient direct substitution trials have been made. If the initial estimate of the recycle stream composition is far different from the expected solution, e.g., zero total rate, a number of trials should first be made with direct substitution. Once started, Broyden acceleration will be applied every trial, without exception.

The Broyden method works best for cases involving multiple recycle steams which are interdependent. PRO/II will apply Broyden acceleration to all recycle streams corresponding to each loop. Caution must be taken when using Broyden acceleration with a user-supplied set of streams to accelerate: if this set does not contain all the tear streams of the loop or loops it belongs to, the inter-dependence may not be well represented by H_k, and therefore, the algorithm may behave poorly.

Reference

Broyden, C.G., 1965, *Math Comp*., 19, pp 577-593.



2.10.4 Flowsheet Control

General Information

PRO/II allows both feedback controllers and multivariable controllers to be included within a flowsheet. These units, which are described in more detail below, allow specifications on process units or streams to be met by adjusting upstream flowsheet parameters. If there is a one-to-one relation between a control variable and a specification, it is best to use a feedback controller. If, on the other hand, several specifications and constraints are to be handled simultaneously, the multivariable controller should be used.

Both the feedback and multivariable controllers terminate when the error in the specifications is within tolerance. By default, the general flowsheet tolerances are used as shown in Table 2.10.4-1.

Table 2.10.4-1: General Flowsheet Tolerances

Temperature	Absolute tolerance of 0.1F or equivalent
Pressure	Relative tolerance of 0.005
Duty	Relative tolerance of 0.005
Miscellaneous	Relative tolerance of 0.01

If the specification does not set a temperature, pressure or duty the ‘‘miscellaneous’’ relative tolerance is used. The tolerances on the controller specifications can be modified either by changing the tolerances at the flowsheet level or directly within the controller unit as part of each SPEC definition.

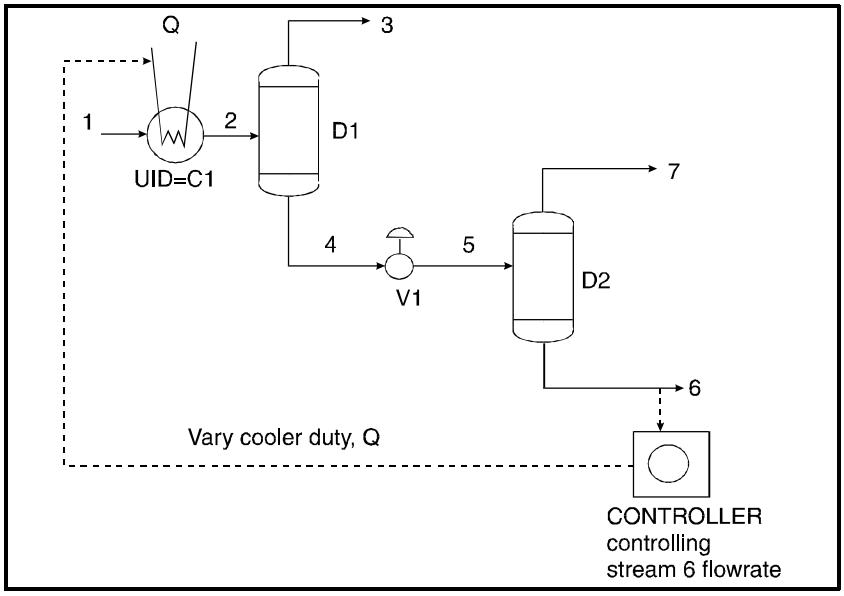
2.10.4.1 Feedback Controller

General Information

The PRO/II CONTROLLER is analogous to a feedback process controller; it varies a particular parameter (control variable) in order to meet a downstream specification on a process unit or stream property or rate. Each CONTROLLER involves exactly one specification and control variable. The specification may be made on a stream property or rate, a unit operating condition or a CALCULATOR result. The control variable can be a stream or unit operating condition, a thermodynamic property or a CALCULATOR result.

Figure 2.10.4.1-1 illustrates a typical controller application. Here, the controller varies the cooler duty in order to achieve a desired flowrate of stream 6.

Figure 2.10.4.1-1. Feedback Controller Example



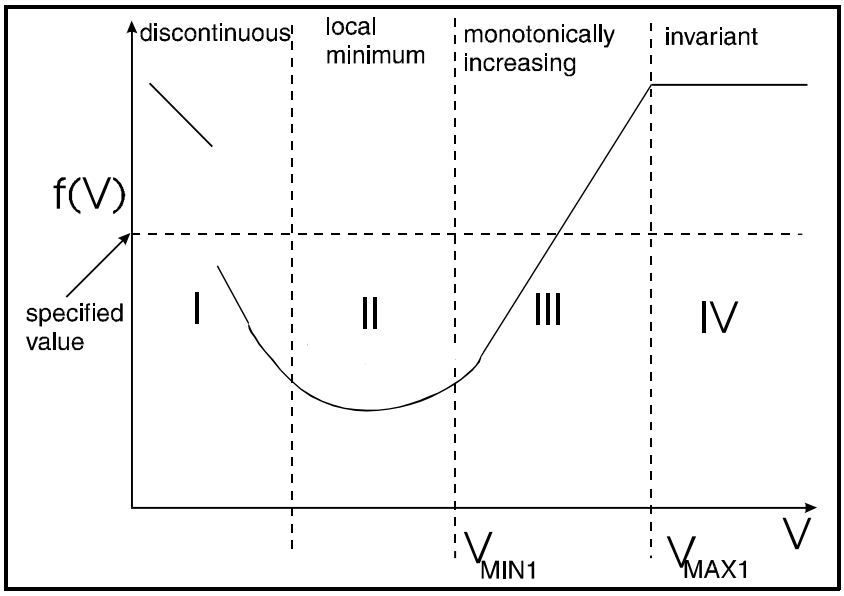
The CONTROLLER uses an iterative search technique to vary the value of the control variable until the specification is satisfied within tolerance. PRO/II automatically creates the computational loop for the CONTROLLER; the units inside this loop are solved repeatedly until the CONTROLLER has converged. For the example in Figure 2.10.4.1-1, units C1, D1, V1 and D2 are solved each time the CONTROLLER varies the cooler duty. The calculations terminate successfully when the flowrate of stream 6 has reached the desired value.

Recommendations

When defining control variables and specifications, it is important to note that the value of a control variable must remain fixed unless it is changed by the CONTROLLER. Typical control variables include inlet feedrates, specified heat duties of heat exchangers and adiabatic flash drums as well as specified reflux ratios of distillation columns. Conversely, the CONTROLLER specifications must be defined as calculated results of the flowsheet simulation e.g. outlet flowrates, column heat duties or temperatures of intermediate streams. However, it is meaningless for the CONTROLLER to specify the temperature of an isothermal flash.

For best performance, the functional relationship between the control variable and the controller specification should be continuous and monotonically increasing or decreasing as illustrated in region III of Figure 2.10.4.1-2. Functions that are discontinuous (region I), exhibit local maxima or minima (region II), or are invariant (region IV) may cause convergence problems. Frequently, these difficulties can be overcome by including upper and/or lower bounds on the control variable to restrict its range (for example V_{MIN1} and V_{MAX1} in Figure 2.10.4.1-2).

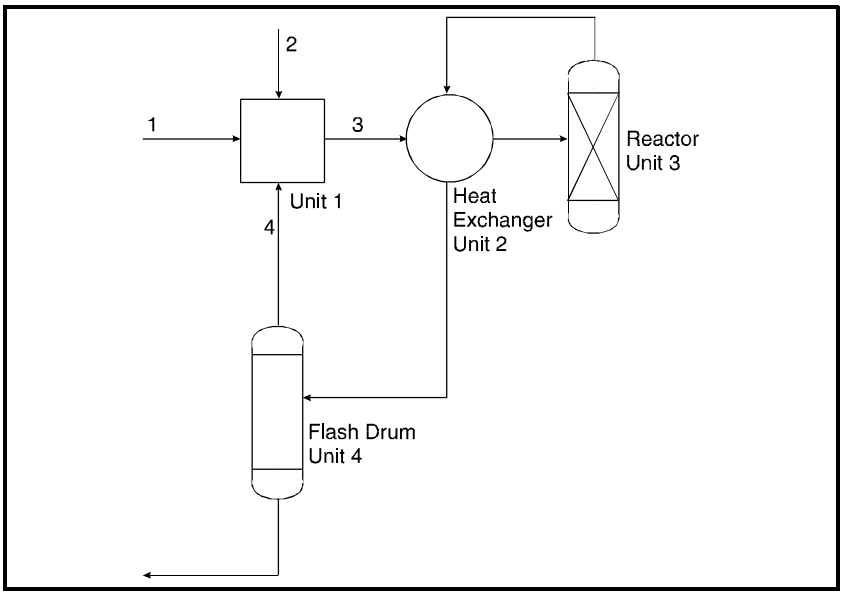
Figure 2.10.4.1-2: Functional Relationship Between Control Variable and Specification



The PRO/II sequencer automatically determines an appropriate calculation sequence for the CONTROLLER loop. When recycle loops are also present, PRO/II determines the loop ordering which allows for most effective flowsheet convergence. To override the default ordering, the desired sequence must be specified explicitly using a SEQUENCE statement. The user should be aware that control loops can significantly increase computational time.

When controllers are placed within recycle loops, careful selection of the controller variable and specification can greatly reduce interference caused by the simultaneous convergence of the two loops. Consider for example the flowsheet shown in Figure 2.10.4.1-3 where stream 2 contains pure reactant A. The rate of stream 2 is to be varied by a CONTROLLER in order to achieve a certain concentration of A in the feed to the reactor.

Figure 2.10.4.1-3: Feedback Controller in Recycle Loop



In this example, the controller would normally be placed inside the recycle loop, after unit 1. Here, the CONTROLLER adjusts the flowrate of stream 2 to achieve the desired concentration in stream 3. The recycle loop is then solved to obtain a new value for the recycle flowrate. This configuration is effective when a good initial estimate for stream 4 is available. If the initial estimate of the flowrate of stream 4 is unavailable, positioning the controller inside the recycle loop may cause the flowrates of stream 2 calculated by the controller to change significantly from one controller solution to the next. This, in turn, causes the recycle loop to experience difficulties. In this situation, it would be more appropriate for the controller to be the outermost loop, allowing the recycle loop to solve and generate an estimate for the flowrate of stream 4 prior to any controller action.

By default, PRO/II prints convergence information at each controller iteration. The controller may fail to converge under the following conditions:

- The specification is not affected by the control variable
- The control variable is at the user-specified maximum or minimum value and the specification is not satisfied
- The maximum number of iterations have been performed
- Three consecutive controller iterations fail to reduce the specification error

For controllers that are not inside other loops, the above conditions cause an error message and all calculations are terminated. For controllers inside recycle or other loops, the calculations are continued until the maximum number of iterations allowed for these outer loops has been performed. If the controller specification is still not met, flowsheet solution then terminates.

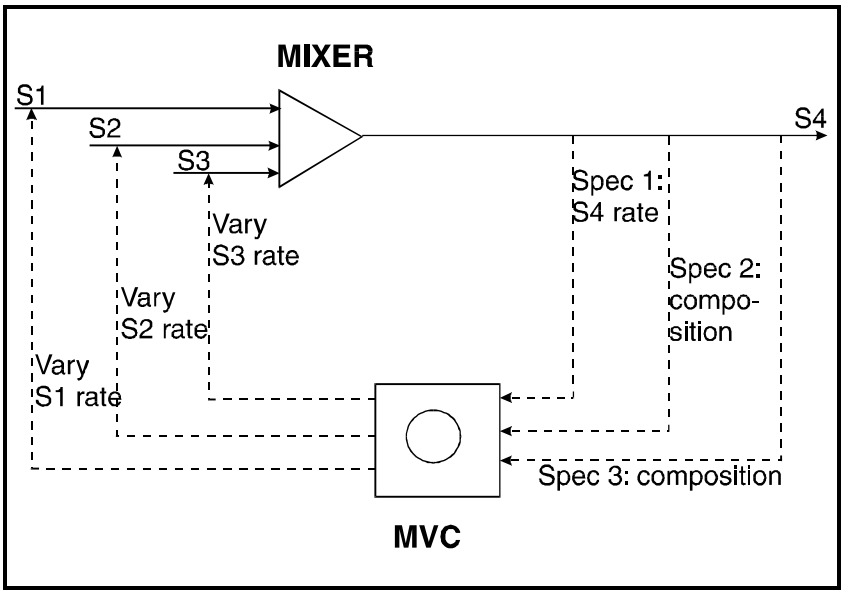
2.10.4.2 Multivariable Feedback Controller

General Information

The multivariable feedback controller (MVC) in PRO/II allows control variables to be varied to satisfy an unlimited number of flowsheet specifications. The specifications can include stream and unit operating conditions as well as CALCULATOR results. The control variables can be defined as stream or unit operating conditions, thermodynamic properties and CALCULATOR results. The number of variables must *equal* the number of specifications. If desired, upper and lower bounds as well as maximum step sizes can also be included for each control variable.

Figure 2.10.4.2-1 shows an example of a simple MVC application. There are three input streams, S1, S2 and S3, all of which contain the three gaseous components C1, C2 and C3 as well as inert gas C4. The flowrates and compositions of the three streams are known. They are mixed to form stream S4 and the MVC is used to specify the total flowrate of S4 as well as the final ratio of C1 to C2 and of C2 to C3. The MVC specifications are to be met by varying the flowrates of the 3 input streams.

Figure 2.10.4.2-1: Multivariable Controller Example



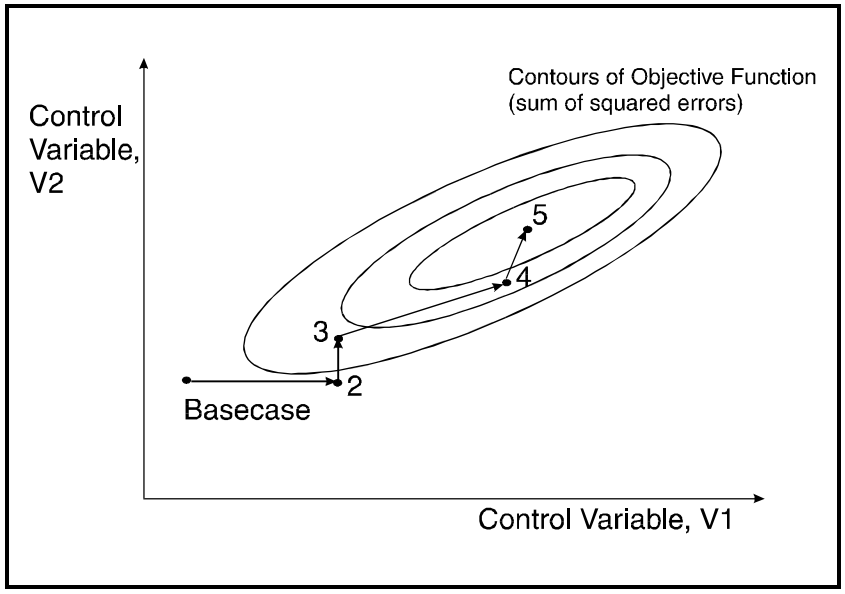
The MVC is essentially an expanded form of the feedback controller. Its main advantage is that it accounts for the interdependence of control variables that are inherently coupled (several control variables affect the same specification). In the above application, for example, each MVC specification is directly affected by all the MVC variables to a greater or lesser extent. Trying to solve the problem using a series of simple feedback controllers will be inefficient and may even result in failure if the changes in the individual controller variables have opposing effects on the specifications. Note though that if the variables are *not* coupled, it is generally more efficient to use separate feedback controllers for each variable and specification pair.

PRO/II automatically creates a loop for the MVC which incorporates all the units that are affected by changes in the MVC variables. The units inside this loop will be solved repeatedly until all the MVC specifications are met within tolerance. If the MVC affects units in a recycle loop, either the MVC loop or the recycle loop may be the outermost one. If the units affected by MVC variables and specs are *all* inside the recycle loop, the MVC will be solved repeatedly every time changes are made to converge the recycle loop. If, on the other hand, MVC specifications or variables affect any unit *outside* the recycle loop, the latter is converged each time the MVC varies a control variable. This choice of sequencing usually results in the lowest solution times. To override the default, the desired sequence must be specified explicitly using a SEQUENCE statement.

The Algorithm

The MVC uses a first-order unconstrained optimization method to simultaneously converge all the specifications. The objective function to be minimized consists of the sum of the squared errors in the specifications. If bounds on the control variables are defined, these are included in the objective function as penalty terms. Figure 2.10.4.2-2 illustrates the solution procedure for an MVC with 2 variables and specifications.

Figure 2.10.4.2-2: MVC Solution Technique



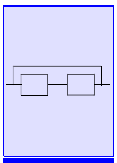
For two variables, the algorithm involves the following steps:

1. Solve the flowsheet at the basecase values of control variables V1 and V2.
2. Increase V1 by 10% (or set V1 equal to EST2, if supplied by the user) and resolve the flowsheet. Compare the value of the objective function at the basecase and at the new point. Move to the new point if the objective function is lower here (point 2 in Figure 2.10.4.2-2).
3. Repeat step 2 for control variable V2.
4. Using the basecase flowsheet solution and those from steps 1 and 2, estimate the derivatives of the objective function with respect to variables V1 and V2 using finite differences.
5. Determine a new search direction using the derivative information at the current point. Here, a hybrid method is used which combines features from Newton-Raphson, Steepest descent and Marquardt methods. Resolve the flowsheet at the new point.
6. If the MVC specifications are not met within tolerance update the matrix of first derivatives using Broyden's method and return to step 5.

The search step determined by the optimizer (step 5 of the above algorithm) is adjusted if it exceeds the user defined STEPSIZES on the variables or if it fails to improve the objective function sufficiently.

For the example in Figure 2.10.4.2-2, a total of 5 MVC cycles is required to reach the solution.

If requested, the MVC prints a detailed convergence history and a series of diagnostic plots. These are intended to help the user determine what corrective action to take when the MVC fails to reach the solution.



2.10.5 Flowsheet Optimization

General Information

The optimization algorithm within PRO/II is a powerful tool which allows the operating conditions of a single unit or an entire process flowsheet to be optimized. Typical applications are the minimization of heat duty or the maximization of profit.

Most generally, the optimization problem can be formulated as:

(1)

minimize	$f(x_1, x_2,...,x_n)$	objective function
such that	$h_i(x_1, x_2,...,x_n) = 0 = 1,...,m_1$	specifications
	$g_i(x_1, x_2,...,x_n) \leq 0 i = 1,...,m_2$	constraints
	$x_{i,mini} \leq x_i \leq x_{i,maxi}$	bounds

where n is the number of variables, m_1 is the number of specifications and m_2 is the number of constraints.

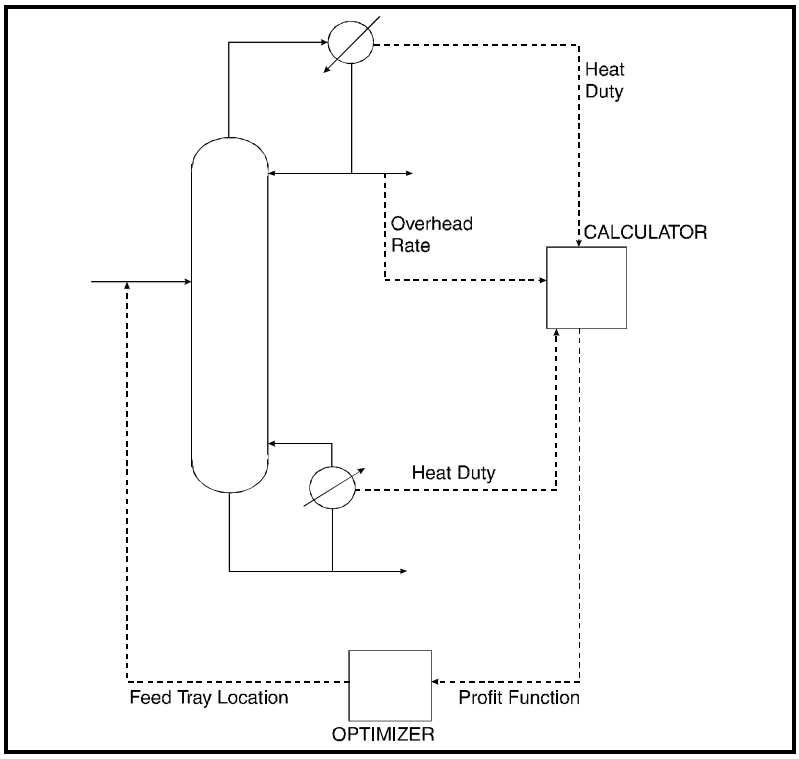
Note: Maximizing f is equivalent to minimizing $-f$.

PRO/II requires an objective function and at least one variable to be defined in the OPTIMIZER unit. In addition, upper and lower bounds must be specified for each variable. If specifications are included, m_1 can be at most equal to the number of variables. The number of constraints which can be defined is independent of the number of variables. There is no hard upper limit on the size of the optimization problem which can be solved.

Typical Application

Figure 2.10.5-1 depicts a typical optimization application:

Figure 2.10.5-1: Optimization of Feed Tray Location



In this example, the OPTIMIZER determines the feed tray location which maximizes a profit function computed by the CALCULATOR. This profit function includes the value of the overhead product less the operating costs of the column. Hence:

(2)

maximize	*Total profit computed by CALCULATOR*	objective function
such that	*Lower limit* ≤ *Feed tray location* ≤ *Upper limit*	bounds

The feed tray location is the optimization variable. The flowsheet has two additional degrees of freedom, the heat duties of the reboiler and the condenser. These are used as flowsheet variables inside the column in order to meet the COLUMN specifications on the purity of the overhead and bottoms products.

Objective Function

Exactly one objective function is required in the OPTIMIZER; it must be defined so that it is the result of a calculation within PRO/II and *not* a value which is fixed by the user.

The OPTIMIZER objective may be either a design or performance objective. It may be expressed as an operational criterion (e.g., maximum recovery or minimum loss) or an economic criterion (e.g., minimum cost or maximum profit). The CALCULATOR can be used to develop more complex objective functions which account for a variety of design and economic factors.

PRO/II Note: For a complete list of the stream and unit operation variables which may be used to define the objective function, see Section 43, *Flowsheet Parameters*, of the *PRO/II Keyword Input Manual*.

Finally, the objective function may also be defined via a user-written subroutine.

Note that the objective function should be *continuous* in the region of interest. The OPTIMIZER will perform best if the objective function shows a good response surface to the variable; it should neither be too flat nor too highly curved. Unfortunately, in practice, many objective functions tend to be quite flat which may cause the optimizer to terminate at different solutions when different starting points are used. These solutions, which are all valid within tolerance will have similar objective function values but the values of the variables may be quite different.

Optimizer Variables

Any flowsheet value which is defined as a fixed input parameter can be used as a variable for the PRO/II optimizer. This includes stream rates or properties, unit operating conditions, thermodynamic properties and CALCULATOR results.

PRO/II Note: For a full list, see Section 43, *Flowsheet Parameters*, of the *PRO/II Keyword Input Manual*.

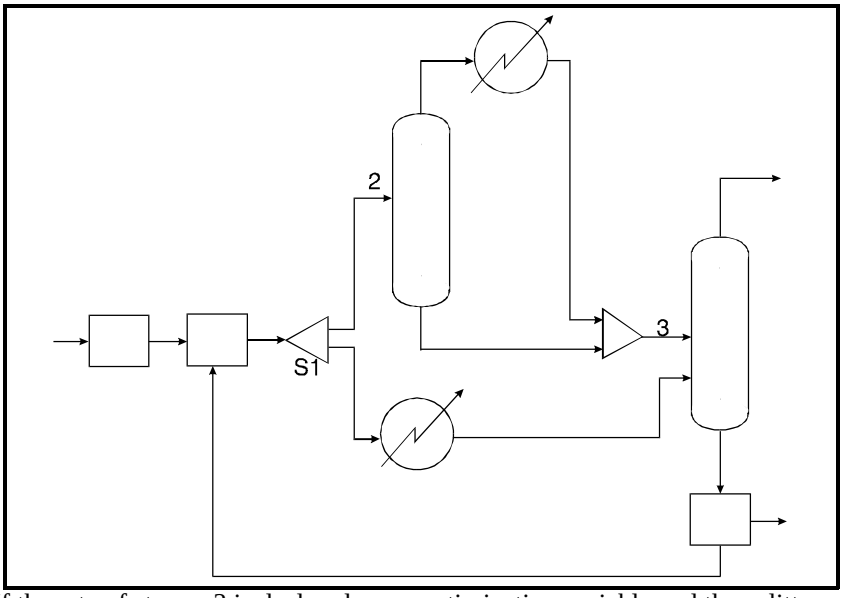
Certain restrictions apply; for example, if the location of COLUMN feeds, draws, heaters or coolers are used as variables within the OPTIMIZER, the rate and/or heat duty cannot also be used.

If the variables to be manipulated by the optimizer are specifications made on the flowsheet basecase, the simplest specifications should be chosen if possible since this speeds up the solution time. For example, suppose a splitter specification is an optimization variable. The basecase specification on the splitter should be a molar rate or ratio, this being the simplest specification possible. The optimizer varies the value of this specification and resolves the flowsheet. Making a more complex specification on the splitter such as the weight rate of a given component in a given product from the splitter and varying this in no way alters the solution to the optimization problem but may increase the computational effort.

The problem may be more acute when column specifications are optimization variables. Here, the simplest specifications, i.e., rate of recovery or reflux should always be chosen since these specifications will make the column easier and faster to solve.

It is important to note that only those flowsheet parameters which are fixed in the basecase can be optimization variables. Thus for an isothermal flash where both temperature and pressure are fixed, both the temperature and pressure may be optimization variables. For an adiabatic flash, on the other hand, the pressure is fixed and the temperature is calculated. Here, it is incorrect to make the temperature an optimization variable. Only the pressure is available for this purpose. In addition, care must be taken that optimization variables are not varied by any other unit. This mistake is especially common when the parameter defined as an optimization variable is already fixed by the remainder of the flowsheet. Consider, for example, the flowsheet in Figure 2.10.5-2.

Figure 2.10.5-2: Choice of Optimization Variables



If the rate of stream 3 is declared as an optimization variable and the splitter S1 is specified with a fixed rate going to stream 2 then, however much the optimizer changes the rate of stream 3, the flowsheet solution does not change. The solution stops in the OPTIMIZER with an error message that another unit is also varying the rate of stream 3. One way to model this particular case would be to specify a splitter fraction on S1 and vary the rate of stream 3. Alternatively, depending on the problem to be solved, the splitter specification can also be varied directly.

PRO/II requires upper and lower bounds to be provided for all variables. For best OPTIMIZER performance, these bounds should be chosen to reflect the actual range within which the flowsheet values are expected to lie. For example, while 0 and 100 degrees Celsius may be a physically valid temperature range for water, 15 and 25 degrees Celsius provide a more meaningful range for the expected temperatures of a cooling water stream.

Specifications and Constraints

Constraints define the domain of acceptable solutions to the optimization problem; that is, they define ranges into which certain flowsheet values must fall (within tolerance) to represent an acceptable solution to the optimization problem. Specifications define specific values within the flowsheet which must be met (within tolerance) to obtain an acceptable solution to the optimization problem.

Constraints and specifications may be made on design or performance values, including values defined by a CALCULATOR unit operation.

PRO/II Note: Section 44, *Specs, Constraints, and Objectives*, of the *PRO/II Keyword Input Manual* discusses the format used to define constraints and specifications. Section 43, *Flowsheet Parameters*, of the *PRO/II Keyword Input Manual* lists all the stream and unit operation variables that can be included in OPTIMIZER constraints and specifications.

Cycles, Trials and Iterations

The optimizer introduces an outer iterative loop in the flowsheet calculation. For the flowsheet in Figure 2.10.5-1, for example, the COLUMN is solved repeatedly until the OPTIMIZER has determined the optimal feed tray location. These iterative loops are referred to as ‘‘cycles’’. Frequently, flowsheets to be optimized also contain recycle streams. Therefore each optimization cycle may involve a number of recycle ‘‘trials’’. Likewise, any column must be converged in a number of ‘‘iterations’’ at every flowsheet pass. This terminology is maintained throughout the PRO/II program and all supporting documentation.

Cycles: Number of optimizer steps (see section on Solution Algorithm below).

Trials: Number of recycle trials in each flowsheet solution. Reset to zero after each flowsheet solution.

Iterations: Number of column iterations per column solution.

For both columns and recycle loops, the maximum number of trials and iterations allowed should be increased to prevent flowsheet failure. While the defaults may be adequate when solving the basecase, the OPTIMIZER may cause the flowsheet to move to a new state where the columns and recycle loops are more difficult to converge.

Recommendations

When solving an optimization problem, the following points should be noted:

- Always solve the base case separately. Check the results carefully to ensure that the problem setup and solution are exactly what is required.
- Carefully select the bounds and constraints to ensure that the flowsheet is physically well-defined over the entire solution space. The flowsheet will not solve if, for example, flowrates or absolute temperatures are allowed to go negative.
- Flowsheet tolerances should be tightened for improved accuracy. This is necessary in order to obtain good first order derivatives and is particularly important when the flowsheet contains columns or recycle loops.

Solution Algorithm

Introduction

PRO/II uses Successive Quadratic Programming (SQP) to solve the nonlinear optimization problem. The algorithm consists of the following steps. To simplify the notation, define $x_k = (x_{1,k}, x_{2,k}, \ldots, x_{n,k})$ as the vector of the optimization variables which define the state of the system.

1. Set the cycle counter k:=1 and solve the flowsheet at x_1.
2. Perturb each optimizer variable by some amount h_i and resolve the flowsheet. Use the base case flowsheet solution and the n additional flowsheet solutions to approximate the first derivatives of the objective function, specifications and constraints *via* finite differences.
3. If $k \geq 2$ use the first order derivatives at the previous and current cycles to approximate the second order derivatives.
4. Solve a quadratic approximation to the nonlinear optimization problem (QP subproblem). This yields a search direction d_k. Set the search step α=1.
5. Solve the flowsheet at $x_{k+1} = x_k + \alpha d_k$.
6. If the flowsheet solution at x_{k+1} is not a sufficient improvement as compared to the flowsheet solution at x_k, reduce the search step α and return to step 4.
7. Let x_{k+1} be the new base case. Set *k:=k+1* and return to step 2.

Various tests are included after the solution of the quadratic approximation (step 3) and after each ‘‘non derivative’’ flowsheet solution (step 4) to determine whether the convergence tolerances are satisfied.

The quadratic programming algorithm used in step 3 automatically determines which of the constraints are binding or active i.e. which of the inequality constraints $g_i(x) \leq 0$ are satisfied as equality constraints $g_{i,A}(x) = 0$ at the current value of the optimizer variables. In addition, the quadratic programming algorithm ensures that the optimizer variables do not exceed their bounds and determines which variables are exactly at a bound (e.g., $x_1 = x_{1,maxi}$).

Note that each optimizer cycle includes steps 2 through 6. If the algorithm has to return to step 4, this is referred to as a line search iteration. Line search iterations are common initially; if line search iterations are necessary close to the solution this frequently indicates that the error in the first order derivatives is too large and the algorithm is having difficulties meeting the convergence tolerances.

Calculation of First-order Derivatives

PRO/II calculates the derivatives of the objective function, specification and constraints with respect to the OPTIMIZER variables using finite differences. A small perturbation is made to each variable separately and the flowsheet is resolved. Each derivative is then calculated by:

$$\frac{\partial f}{\partial x_i} \approx \frac{f(x_i + h_i) - f(x_i)}{h_i} \qquad (3)$$

To obtain the best derivative information, the step size h_i for each variable x_i should be small enough so that the higher order terms which are neglected in the above formula are minimized. However, if h_i is too small, the derivatives will be dominated by flowsheet noise. The accuracy of the derivatives can be improved by tightening the flowsheet tolerances and by using the appropriate perturbation steps.

By default, the perturbation steps are calculated as 2% of the range of each of the variables (this is increased to 5% if NOSCALE is entered on the OPTPARAMETER statement). The user can override this default by entering values for APERT or RPERT. If the functions and derivatives are well-behaved, the ''ideal'' perturbation size is given by:

$$h_i = \sqrt{\varepsilon_R}\ \left| x_{i,typical} \right| \qquad (4)$$

where:

ε_R = the relative accuracy with which the functions are evaluated.

For simple functions this is on the order of machine precision (~ 10^{-6}); for complex flowsheets with sufficiently tight tolerances the relative accuracy is on the order of 10^{-3} to 10^{-4}.

To aid the user in selecting appropriate stepsizes, a full diagnosis is printed when the maximum number of OPTIMIZER cycles is set equal to 2. In addition to the forward difference formula given above, the derivatives are also calculated using backward differences and central differences.

The information shown in Table 2.10.5-1 is then displayed for each variable for the objective function and each specification and constraint.

Table 2.10.5-1: Diagnostic Printout

Sign (backward,central,forward)	- or 0 or +
Effect	none or low or high
Maximum deviation	percentage
Current perturbation size	value
Suggested perturbation size	value

Unless a variable has no effect, the first line displays the sign of the backward, central and forward derivatives. If the maximum difference between the central derivative and forward or backward derivatives is greater than 1%, it is reported on line 3. The perturbation size should be chosen so as to minimize this difference. The current value of the absolute perturbation is reported on line 4 and a suggested perturbation, calculated assuming that the accuracy of the flowsheet solution is 10^{-4}, is printed on the last line. Note that this value is only intended as a guideline; the change in the maximum deviation should be monitored when the perturbation size is modified. Note also that if the magnitude of a variable changes by several orders of magnitude, the perturbation size determined at the initial point will no longer be appropriate.

To ensure consistent flowsheet solutions it may also be necessary to invoke the COPY option (an OPTPARAMETER keyword). Here, the entire PRO/II database is stored which allows the flowsheet variables to be initialized identically for each perturbation evaluation rather than at the final value from the previous perturbation.

Bounds on the Variables

For best optimizer performance it is very important to supply appropriate upper and lower bounds for each variable. The bounds are used for the automatic scaling of the variables. As discussed previously, they are also used to determine the default perturbation size and, finally, they may also affect the magnitude of the optimizer steps during the first three cycles (see the section following).

STEP Sizes

By default, the OPTIMIZER variables are not allowed to move more than 30, 60 and 90 percent to their upper or lower bound during optimization cycles 1, 2 and 3, respectively. This is intended as a ‘‘safety feature’’; it prevents the optimizer from moving too far, particularly when the derivatives are inaccurate. The STEP keyword is used to override this default by providing an absolute limit for the maximum change in a variable during one optimization cycle. Providing a value for STEP which is larger than MAXI-MINI for a particular variable allows that variable to move through its full range at every optimization cycle.

If the OPTIMIZER contains more than one VARY statement, the changes in the variables determined in step 3 of the above algorithm will *all* be reduced by the *same* factor until all the variables are within the limits imposed by the individual STEPSIZEs. Hence, the *relative* change in the variables is not affected by the STEPSIZE on each variable.

Termination Criteria

The following conditions are tested at every optimizer cycle:

1. Is the relative change in the objective function at consecutive cycles less than 0.005 (or the user defined value RTOL for the objective function)?
2. Is the relative change in each variable at consecutive cycles less than 0.0001 (or the user defined values RTOL for each variable)?
3. Has the maximum number of cycles been reached?
4. Does the scaled accuracy of the solution fall below 10^{-7} (or the user defined value SVERROR)? The scaled accuracy, which is also known as the Kuhn-Tucker error, is calculated from:

$$KTE = \nabla f^T d + \sum_i \left|\lambda_i h_i\right| + \sum_i \left|\mu_i g_i\right| \qquad (5)$$

where:

∇f = a vector which contains the first derivatives of the objective function

d = the search direction from the QP subproblem

h *and* g = specifications and constraints, respectively.

The weights on the specifications and constraints, λ and μ, are determined automatically when the QP subproblem is solved (step 3 in the algorithm previously described). These weights are referred to as multipliers or shadow prices (see the following section).

If *none* of the above conditions are satisfied, the optimizer continues to the next cycle. If *at least one* of conditions 1 to 4 is satisfied, the following conditions are also tested.

5. Is the relative error for each specification less than 0.001 (or the user defined value RTOL or ATOL for each specification)?
6. Is the relative error for each constraint less than 0.001 (or the user defined value RTOL or ATOL for each constraint)?

If both 5 and 6 are satisfied, the OPTIMIZER terminates with the message SOLUTION REACHED. If the relative error for any specification or constraint is greater than the required tolerance, the OPTIMIZER will terminate with SOLUTION NOT REACHED.

The optimization problem may also fail for one of the following reasons:

- Another unit in the flowsheet may fail to converge.
- The number of column, controller or recycle loops which is allowed is insufficient.
- The optimization problem is infeasible.

Postoptimality Analysis – Shadow Prices

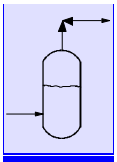
Once the flowsheet optimization has converged and the appropriate operating conditions have been determined, the *shadow prices* or Lagrange multipliers can be used to assess the sensitivity of the objective function to the specifications, constraints and bounds. These values, which are calculated automatically by the optimization algorithm are reported in the output report if OPRINT=ALL is selected on the OPTPARAMETER statement. The signs of the multipliers follow the following convention:

- If the multiplier of a specification or constraint is *positive*, then *increasing* the corresponding MINI, MAXI or VALUE will *increase* the value of the objective function.
- If the multiplier of a specification or constraint is *negative*, then *increasing* the corresponding MINI, MAXI or VALUE will *decrease* the value of the objective function.

In addition, the magnitude of the shadow prices indicates which specifications and constraints have the greatest effect on the optimal solution.

References

1. Fletcher, R., 1987, Practical Methods of Optimization, Wiley.
2. Gill, P.E., Murray, W., and Wright, M.H., 1981, Practical Optization, Academic Press.



2.11 Depressuring

General Information

All unit operation calculation methods described in previous chapters of this manual relate to process units operating under steady-state conditions. PRO/II also provides a model for one unsteady-state process unit — the depressuring unit.

This unit operation may be used to determine the time-pressure-temperature relationship when a vessel containing liquid, vapor, or a vapor-liquid mixture is depressured through a relief or control valve. The user may input the valve flow characteristics. This unit operation also finds application for problems relating to refrigeration requirements in storage vessels. Product streams may be generated as a user option, but the calculations are not performed until output time. A heat input may also be described by the user to simulate the pressuring of the vessel by a fire or other means.

Theory

The depressuring unit is shown in Figure 2.11-1. The depressuring calculations begin by mixing the feed streams adiabatically to give the composition, $x_{i,0}$, temperature, T_0, and pressure P_0 of the vessel at time t=0. The initial composition of the liquid and vapor inside the vessel is calculated following the guidelines below.

If a liquid holdup is specified:

- For a mixed-phase feed, the composition of the liquid phase, will be set equal to the composition of the liquid portion of the feed, and the vapor-phase composition set equal to the feed vapor composition.
- For a liquid-phase feed, then the initial vapor composition in the vessel will be set equal to the vapor in equilibrium with the feed liquid at its bubble point temperature.

Note: For a vapor only feed, PRO/II will give an error message if a liquid holdup is specified.

After the initial composition of the vapor and liquid portion of the vessel contents is determined, the initial total number of moles for each component, $F_{i,0}$, in the vessel is calculated using:

$$F_{i,0} = x_{i,0}^{L} V_0^{L} \rho_0^{L} + x_{i,0}^{V} V_0^{V} \rho_0^{V} \quad (1)$$

where:

$F_{i,0}$ = moles of component i at time t=0

$x_{i,0}^{L}$ = mole fraction of component i in liquid

$x_{i,0}^{V}$ = mole fraction of component i in vapor

V_0^{L} = initial liquid volume in vessel

V_0^{V} = initial vapor volume in vessel

If no liquid holdup is specified:

- The composition of the vessel contents is set equal to the composition of the feed, and the temperature and pressure of the vessel are set equal to that of the feed stream. The total number of moles of each component in the vessel at time t=0, $F_{i,0}$, is calculated using:

$$F_{i,0} = x_i^{feed} V_0 \rho_{f,mix} \quad (2)$$

where:

$F_{i,0}$ = moles of component i at time t=0

x_i^{feed} = mole fraction of component i in feed

V_0 = volume of vessel

$\rho_{f,mix}$ = mixture density of feed stream

Calculating the Vessel Volume

The volume of the vessel holdup liquid is calculated for spherical, vertical cylindrical, or horizontal cylindrical vessels, using the following relationships:

Horizontal Cylinder Vessel

$$V_v = \left(\pi r^2 L + 2V_{end}\right) V_{fac} \quad (3)$$

where:

r = radius of vessel

L = tangent to tangent vessel length

V_{fac} = volume factor which corrects for pipes and fittings

V_{end} = end cap volume, which is given by:

$$V_{end} = \frac{3}{8}\pi r^3 \quad (4)$$

The optional user-supplied volume correction factor, V_{fac}, defaults to a value of 1.0, if not supplied.

Vertical Cylinder Vessel

$$V_v = \left(\pi r^2 h + 2V_{end}\right) V_{fac} \quad (5)$$

where:

r = radius of vessel

h = tangent to tangent vessel height

The end cap volume, V_{end}, is again given by equation (4) above.

Spherical Vessel

$$V_v = \frac{4}{3}\pi r^3 V_{fac} \quad (6)$$

Valve Rate Equations

All the valve equations are based on *vapor flow only* through the valve. The valve upstream pressure is assumed to be the same as the vessel pressure.

For supersonic flow, the pressure drop across the discharge valve, ΔP, should satisfy the relationship:

$$\Delta P \geq 0.5 C_f^2 P_1 \quad (7)$$

where:

C_f = critical flow factor, dimensionless

ΔP = actual pressure drop = P_1 - P_2, psia

P_1 = upstream pressure, psia

P_2 = downstream pressure, psia

The valve rate for supersonic flow is given by:

$$W = 2.8\, C_v\, C_f\, P_1 \sqrt{G_f} \quad (8)$$

where:

W = vapor flow rate through valve, lbs/hr

C_v = valve flow coefficient, dimensionless

G_f = specific gravity at temperature T(^{o}R)

The gas specific gravity can be written as:

$$G_f = \frac{520\, MW}{MW_{air}\, T} \quad (9)$$

where:

MW = molecular weight of discharge stream

MW_{air} = molecular weight of air

T = temperature of stream, ^{o}R

The stream molecular weight is given by:

$$MW = zRT\frac{\rho_v}{P_i} \tag{10}$$

where:

z = gas compressibility factor

R = gas constant = 1.98719 BTU/lb-mol°R

ρ_v = vapor density, lb/ft^3

Substituting equations (9) and (10) in equation (8) gives the following expression for the vapor rate through a valve under supersonic flow conditions:

$$W = C_1\sqrt{P_1\,\rho_v} \tag{11a}$$

where:

$$C_1 = 2.8C_v\,C_f\sqrt{\frac{520zR}{MW_{air}}} \tag{11b}$$

For subsonic flow, the pressure drop across the valve must satisfy:

$$\Delta P < 0.5C_f^2\,P_1 \tag{12}$$

The valve rate for subsonic flow is given by:

$$W = 3.22C_v\sqrt{\Delta P P_1\,G_f} \tag{13}$$

Again, substituting equations (9) and (10) into (13), the valve rate for subsonic flow becomes:

$$W = C_1\sqrt{\Delta P\rho_v} \tag{14a}$$

where:

$$C_1 = 3.22C_v\sqrt{\frac{520zR}{MW_{air}}} \tag{14b}$$

The constant C_1 has units of :

(weight/time) / (pressure·weight / volume)$^{0.5}$.

Alternatively, the user can specify a constant discharge rate:

$$W = Constant \tag{15}$$

The user may also specify a more general valve rate formula:

$$W = AC_f\,C_v\,Y_f\sqrt{P_1\,\rho_v} \tag{16}$$

where:

A = a constant with units of (weight·volume/pressure· time^2)$^{1/2}$.

Values for the constant A in equation (16) in English, SI, or Metric units are given in Table 2.11-1.

Table 2.11-1: Value of Constant A

Dimensional Units	Value of A
English	38.84
SI	1.6752
Metric	16.601

Y_f and Y are given by:

$$Y_f = Y - 0.148Y^3 \qquad (17)$$

and,

$$Y = \frac{1.63\left[\frac{\Delta P}{P_1}\right]^{0.5}}{C_f} \qquad (18)$$

If Y > 1.5, Y_f is not calculated by equation (17), but is instead set equal to 1.0.

The control valve coefficient, C_v, is defined as ‘‘the number of gallons per minute of water which will pass through a given flow restriction with a pressure drop of 1 psi.’’. This means that the value of C_v is independent of the problem input units.

Heat Input Equations

The heat flow between the depressuring vessel and a heat source or sink may be defined using one of four types of heat input models.

User-defined Model

This heat model is given by:

$$Q = C_1 + C_2 t + C_3 (C_4 - T_t^v) + C_5 \frac{V_t}{V_i} \qquad (19)$$

where:

Q = heat duty in millions of heat units/time

C_1, C_2, C_3, C_4, C_5 = constants in units of millions of heat units/time

T_t^v = vessel temperature at time t

V_t = volume of depressuring vessel at time t

V_i = volume of depressuring vessel at initial conditions

If values for the constants are not provided, the general heat model defaults to Q = 0.0, i.e., to adiabatic operation.

API 2000 Model

This heat model is recommended for low pressure vessels and is given by:

$$Q = C_1 (A_t)^{C_2} \quad (20)$$

where:

C_1, C_2, = constants whose values are given in Table 2.11-2

A_t = current vessel wetted area = A_i

A_i = initial wetted area, ft^2

Table 2.11-2: Value of Constants C_1, C_2

For A_t	C_1	C_2
20 - 200	20000	1.000
201 - 1000	199300	0.566
1001 - 2800	963400	0.338
> 2800	21000	0.820

A dimensionless area scaling factor may also be used with the API 2000 heat model. If a scaling factor, A_{fac}, is specified, the current vessel wetted area is not equal to the initial wetted area, but is instead calculated using:

$$A_t = A_i A_{fac} \frac{V_t}{V_i} \quad (21)$$

APISCALE Model

This heat model is similar to the API 2000 heat model, except the heat duty is scaled and is given by:

$$Q = C_1 (A_t)^{C_2} \frac{V_t}{V_i} \quad (22)$$

Again, an area scaling factor may or may not be specified. If A_{fac} is used, A_t is given by equation (17). If A_{fac} isn't specified, A_t is set equal to the initial wetted area.

API RP520 Model

This heat model applies to uninsulated vessels above ground level and is the recommended model for pressure vessels. The heat model is given by:

$$Q = 21000 (A_t)^{0.82} \quad (23)$$

Again, an area scaling factor may or may not be specified. If A_{fac} is used, A_t is given by equation (17). If A_{fac} isn't specified, A_t is set equal to the initial wetted area.

API RPSCALE Model

This heat model is similar to the API RP520 model, but with scaling applied. It is given by:

$$Q = 21000\,(A_t)^{0.82}\,\frac{V_t}{V_i} \qquad (24)$$

Again, an area scaling factor may or may not be specified. If A_{fac} is used, A_t is given by equation (21). If A_{fac} isn't specified, A_t is set equal to the initial wetted area.

Fire Relief Model

The fire relief model is given by:

$$Q = C_1\,C_2\,(A_t)^{C_3} \qquad (25)$$

where:

C1, *C2*, *C3* = user-supplied constants

Gas Blowdown Model

The gas blowdown model assumes an external heat input to the vessel metal followed by transfer of heat from the vessel metal to the gas. Initially, the vessel temperature is taken to be the same as the gas temperature. The external heat input is then calculated from:

$$Q_{ext} = C_1 + C_2 t + C_3\,(C_4 - T_{wall}) + C_5\,\frac{V_t}{V_i} \qquad (26)$$

The heat transfer to the fluid inside the vessel is computed using:

$$Q_{int} = h_v\,A_{vap}\,\Delta T + h_l\,A_{liq}\,\Delta T \qquad (27)$$

$$\Delta T = T_{wall} - T_{fluid} \qquad (28)$$

where:

h_v = heat transfer coefficient between the vessel and the vapor phase of the fluid

A_{vap} = area of vapor phase in vessel

T_{fluid} = temperature of fluid in the vessel at time t

h_l = heat transfer coefficient between the vessel and the liquid phase of the fluid

A_{liq} = area of liquid phase in vessel

The gas is depressured isentropically using either a user-defined isentropic efficiency value or the default value of 1.0. For each time interval, the heat transfer from the vessel is calculated by using the Nusselt heat transfer correlations. The heat transfer coefficient between the vessel and the vapor phase of the fluid, h_v, is determined using:

$$h_v = \frac{0.13 k_v (N_{Gr} N_{Pr})^{1/3} h_{fac}}{r} \quad (29)$$

where:

k_v = thermal conductivity of vapor phase

N_{Gr} = dimensionless Grashof number

N_{Pr} = dimensionless Prandtl number

h_{fac} = heat transfer coefficient factor (=1.0 by default)

The Grashof and Prandtl numbers are given by the following relationships:

$$N_{Gr} = \frac{r^3 \rho_v^2 \beta g_c \Delta T}{\mu_v^2} \quad (30)$$

$$N_{Pr} = \frac{cp_v \mu_v}{k_v} \quad (31)$$

where:

β = volumetric coefficient of thermal expansion, 1/°F

g_c = acceleration due to gravity

μ_v = viscosity of vapor

ΔT = T_{wall} - T_{fluid}

cp_v = heat capacity of vapor

The heat transfer coefficient between the vessel and the liquid phase of the fluid, h_l, is determined in a similar manner using the following relationships.

$$h_l = \frac{0.13 k_l (N_{Gr} N_{Pr})^{1/3} h_{fac}}{r} \quad (32)$$

where:

k_l = thermal conductivity of liquid phase

The Grashof and Prandtl numbers are given by the following relationships:

$$N_{Gr} = \frac{r^3 \rho_l^2 \beta g_c \Delta T}{\mu_l^2} \quad (33)$$

$$N_{Pr} = \frac{cp_l \, \mu_l}{k_l} \tag{34}$$

where:

μ_l = viscosity of liquid

cp_l = heat capacity of liquid

The change in the wall temperature, ΔT_{wall}, is determined from the isentropic enthalpy change and the heat transferred to the gas from the wall, i.e.,

$$\Delta T_{wall} = \frac{Q_{ext} \, \Delta t - (\Delta q_{fluid} - q_{isen}) \, M_{\Delta t}}{W_{vess} \, cp_{vess}} \tag{35}$$

where:

Δq_{fluid} = change in specific enthalpy of the fluid, BTU/lb-mole

Δq_{isen} = isentropic specific enthalpy change as the gas expands

$M_{\Delta t}$ = moles of gas depressured in time period Δt, lb-mole

W_{vess} = weight of depressuring vessel, lb

cp_{vess} = heat capacity of depressuring vessel, BTU/lb-°F

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